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REFINING OF MILITARY JET FUELS FROM SHALE OIL PART II  
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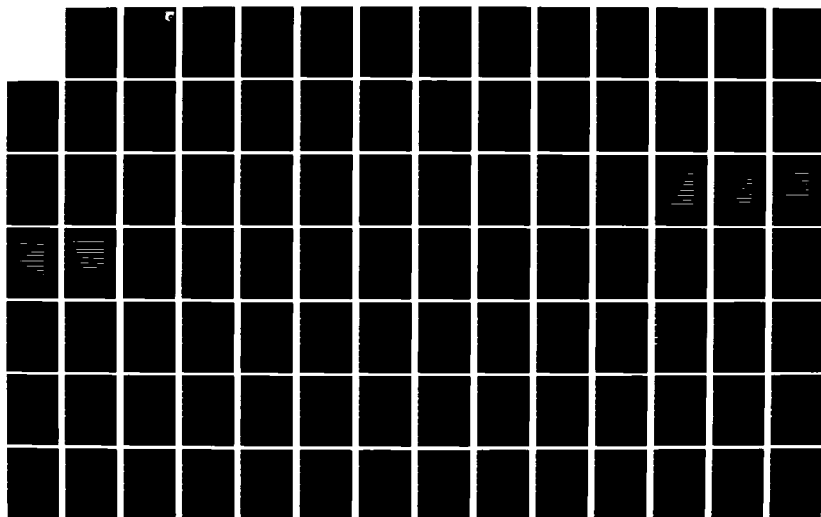
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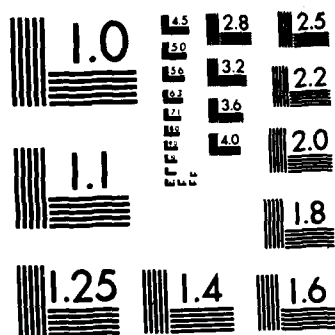
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Part II, Vol III



REFINING OF MILITARY JET FUELS FROM SHALE OIL

Part II, Vol III  
Above Ground Shale Oil Process Data

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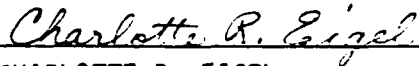
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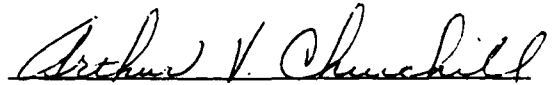
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This technical report has been reviewed and is approved for publication.



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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Phase II work performed was directed toward the completion of two primary tasks. Task I under this phase was directed at evaluating the effect of operating conditions on material quality, energy balances, product composition and economics. Task II was directed at obtaining scale-up data for those unit operations of the Phase I process requiring laboratory data to confirm preliminary estimates. This volume presents the data generated on the above-ground crude shale oil, retorted at the Paraho Anvil Points facility.		

# FOREWORD

This project was sponsored by the U.S. Air Force Wright Aeronautical Laboratories (AFWAL), Air Force Systems Command, under Contract No. F33615-78-C-2080. The work herein was performed during the period June 15, 1979 to October 30, 1980 under Program Elements 62203F and 63215F, Work Units 30480504 and 24800004, respectively. A discussion of the entire Ashland effort under this contract can be found in a series of six reports (AFWAL-TR-81-2056) entitled "Refining of Military Jet Fuels from Shale Oil," Parts I, II, III, and IV (Part II consists of three volumes). This report is Volume III of Part II which describes the evaluation, via the EXTRACTACRACKING Process, of the above-ground Paraho crude shale oil. The cognizant Air Force Project Scientist was Dr. Ronald D. Butler. We must also give recognition to Carolyn Honaker for her assistance in preparing this report.

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## ABBREVIATIONS

A	Aromatics
Acid Str	Acid Strength
APL	Aero Propulsion Laboratory
AFWAL	Air Force Wright Aeronautical Laboratories
API	American Petroleum Institute
AQ	Aqueous
AR SAT	Aromatic Saturation Unit
As	Arsenic
ASTM	American Society for Testing Materials
bbl	Barrel
BN	Basic Nitrogen
$\frac{(\text{BN})}{(\text{TN})_p}$ $\frac{(\text{BN})}{(\text{TN})_f}$	Ratio of Basic Nitrogen over Total Nitrogen in Product to Basic Nitrogen over Total Nitrogen in Feed
BPD	Barrels per Day
BR NO.	Bromine Number
BS&W	Bottoms, Sediment and Water
BTU	British Thermal Unit
°C	Degrees Celsius
C	Carbon or Heteroatom Concentration
C <sub>1</sub>	Methane
C <sub>2</sub>	Ethane
C <sub>3</sub>	Propane
C <sub>3</sub> <sup>=</sup>	Propylene

ABBREVIATIONS (CONT'D)

n-C <sub>4</sub>	Normal Butane
i-C <sub>4</sub>	Isobutane
C <sub>4</sub> <sup>=</sup>	Butylene
C <sub>5</sub>	Pentane
C <sub>5</sub> 's	Pentane and Pentenes
C <sub>5</sub> <sup>+</sup>	Compounds Heavier than Pentane in Gas Streams
C <sub>6</sub>	Hexane
C/H	Carbon to Hydrogen Ratio
cc	Cubic Centimeters
cm	Centimeter
CO	Carbon Monoxide or Cycle Oil
C/O	Catalyst-to-Oil Ratio
COHT	Cycle Oil Hydrotreater
Co/Mo or CoMo	Cobalt Molybdate Catalyst
Cont. Time	Contact Time
Conv.	Conversion
CR	Cracked
CSHT	Crude Shale Hydrotreater
cSt	Centistoke
CW	Cooling Water
E	Activation Energy
EP	End Point in a Distillation

ABBREVIATIONS (CONT'D)

EXTD	Extracted
°F	Degrees Fahrenheit
FCC	Fluid Catalytic Cracker
FCR	Fluid Catalytic Reactor
Fe	Iron
FI	Flow Indicator
FIA	Fluorescent Indicator Adsorption - Test Method to Determine Hydrocarbon Types
g	Gram
GC	Guardcase Hydrotreater
GC-1	Guardcase Study on In Situ Shale Oil
Gms	Grams
H <sub>2</sub>	Hydrogen
HC	Hydrocarbon
HC/N	Ratio of Hydrocarbons to Nitrogen
Hg	Mercury
Hr or hr	Hours
Hr <sup>-1</sup> or hr <sup>-1</sup>	Inverse Hours
H <sub>2</sub> S	Hydrogen Sulfide
Hydrog.	Hydrogenated



ABBREVIATIONS (CONT'D)

IBP	Initial Boiling Point
I.D.	Inside Diameter
in	Inches
JP-4	Military Specification MIL-T-5624K Turbine Fuel
JP-5	Military Specification MIL-T-5624H Turbine Fuel
JP-7	Military Specification MIL-T-38219 Turbine Fuel
JP-8	Military Specification MIL-T-83133 Turbine Fuel
$K_0$	Rate Constant
lb	Pound
LCO	Light Cycle Oil
LHSV	Liquid Hourly Space Velocity
LPG	Liquefied Petroleum Gas
LV%	Liquid Volume Percent
MAT	Microactivity Test
MAV	Maleic Anhydride Value
MAX	Maximum
mg	Milligram
MIN or min	Minimum
min	Minute

ABBREVIATIONS (CONT'D)

ml	Milliliter
mm	Millimeter
MT'L	Material
N	Nitrogen
N <sub>O</sub> or N <sub>f</sub>	Nitrogen in Feed
N <sub>p</sub>	Nitrogen in Product
Na <sup>+</sup>	Sodium Ion
Na <sub>2</sub> CO <sub>3</sub>	Sodium Carbonate
NaOH	Sodium Hydroxide
NH <sub>3</sub>	Ammonia
Ni	Nickel
Ni/Mo or NiMo	Nickel Molybdate Catalyst
NO.	Number
NO <sub>x</sub>	Oxides of Nitrogen
n-PARAFFIN	Normal Paraffin
O	Olefins
ON SPEC	Meeting Specifications
OXY	Test Series on In Situ Shale Oil
P	Pressure
(P + N)	Paraffins and Naphthenes
PHO	Test Series on Above-Ground Shale Oil

ABBREVIATIONS (CONT'D)

PI	Pressure Indicator
PID Controller	Proportional-Integral-Derivative Controller
ppb	Parts per Billion
ppm	Parts per Million
psia	Pounds of Force per Square Inch Absolute
PSIG or psig	Pounds of Force per Square Inch Gauge
Pt/Al	Platinum/Aluminum Catalyst
Pt/Re	Platinum/Rhenium Catalyst
PV	Parameter Variation
R	Gas Constant
°R	Degrees Rankine
RAFF	Raffinate
RAMS C	Ramsbottom Carbon
RCVY	Recovery
R&D	Research & Development
REF	Reformer
REGEN	Regenerator Section of FCC
RVP	Reid Vapor Pressure
S	Sulfur
SAT	Saturates
SCFB	Standard Cubic Feet per Barrel
SCFH	Standard Cubic Feet per Hour
SIM-D	Simulated Distillation

ABBREVIATIONS (CONT'D)

SR	Straight Run
SS	Stainless Steel
SU or SUS	Saybolt Universal Seconds
TBP	True Boiling Point
TEMP or t	Temperature
TIC	Temperature Indicator and Controller
V	Vanadium
VIS	Viscosity
VOL	Volume
VOL %	Volume Percent
WBS	Work Breakdown Structure
WHSV	Weight Hourly Space Velocity
WT	Weight
WT %, % W, or % WT	Weight Percent

## SYMBOLS

=	Equals
+	Positive, plus, or greater than as in 600°F+
-	Negative, minus, or less than as in -600°F
%	Percent
>	Greater Than
<	Less Than
"	Inches
#	Number or Pound
Δ	Difference

## SUMMARY

Above-ground shale oil, retorted at the Paraho Anvil Points Facility, has been evaluated as feedstock for upgrading to turbine fuels via the EXTRACTACRACKING process. The complete process evaluation sequence was completed on a laboratory basis.

The Paraho oil was shown to be an acceptable EXTRACTACRACKING feedstock. JP-4, JP-5 and JP-8 turbine fuel samples were prepared from this material and submitted for evaluation.

SECTION I  
INTRODUCTION

On February 15, 1979, Ashland Petroleum Company Research and Development Department began work under contract F33615-78-C-2080, An Exploratory Research and Development Program Leading to Specifications for Aviation Turbine Fuel from Whole Crude Shale Oil. This program, funded by the Department of Defense, is designed to evaluate the EXTRACT-ACRACKING process as a potential improvement in shale oil refining technology.

EXTRACTACRACKING is a novel, integrated process developed by Ashland Petroleum Research composed of a unique combination of hydrotreating, fluid cracking, extraction and product upgrading sequences. The process is designed to reduce costs by minimizing hydrogen consumption and operating severity requirements. A more detailed discussion of the process is contained in Volume I of this report.

Phase I of this study was performed as a preliminary economic analysis of the process and was completed on June 15, 1979. Phase II was performed to evaluate process parameters in order to define optimum operating regions based on cost and to prepare five 500-ml samples of aviation turbine fuel from the complete process. Data obtained during Phase II is reported in three volumes:

- Volume I: Interim Technical Report
- Volume II: In Situ Shale Oil Data Book
- Volume III: Above-Ground Shale Oil Data Book

This volume collects all data obtained during processing of above-ground shale oil during Phase II, for the period June 15, 1979 through October 1, 1980.

Work in Phase II was broken into major functional areas for completion. Since EXTRACTACRACKING is an integrated process, both screening and sample production studies for further processing were required. Where possible, the program was defined such that small sample quantities could be utilized.

Initial rapid parameter screening tests were performed for the crude shale hydrotreater module. These tests comprised a wide range of operating severities over two catalyst types. Products from these screening tests were fractionated and selected bottoms samples evaluated for FCC performance on the microactivity unit (MAT). Some samples were also utilized for MAT work from the M-Series sample production material.

Results from preliminary screening were utilized to define anticipated required operating severities for crude hydrotreater and FCC units. Those conditions were then utilized for production of the M-Series samples which were processed through the entire flow sheet.



The M-Series data, plus the earlier screening data, were utilized to define preliminary optimum operating regions by the process computer model developed during Phase I. Conditions indicated by that preliminary optimization were utilized for preparation of the listed PHO sample, which also was processed through the entire processing sequence.

All data obtained for above-ground shale oil is contained in this volume. Very little effort has been made herein to define module interactive or other effects; these will be discussed fully in Volume I. The purpose of this volume is to delineate data bases and procedures for further evaluation.

## SECTION II

### CRUDE SHALE ANALYSIS

#### SUMMARY

Two types of shale oils, in situ and above-ground retorted, have been characterized by fractionation and subsequent analysis of the fractional products. These efforts were required as outlined for fulfillment of Phase II objectives in the Military Jet Fuels from Shale Oil Program.

The shale oils, Occidental Petroleum's in situ oil produced during Retort #6 and Paraho above-ground retorted oil obtained from the Anvil Point facility, were handled identically and simultaneously.

#### OBJECTIVE

The objective is to provide a detailed definition of physicochemical properties for the shale oils under investigation. This data becomes the basis for all subsequent observations regarding the effectiveness of EXTRACTACRACKING process modules.

#### MECHANICAL DESCRIPTION

The fractionation of each oil sample was accomplished in two increments of work. Each sample was first distilled in increments to an endpoint of approximately 600°F, after which the >600°F boiling range liquids were transferred to an alternate apparatus and the distillation was continued. The equipment used will be described below.

A Podbielniak Semi-Cal model 3650 fractional distillation apparatus was utilized for the low temperature portion of the fractionation. This column is a completely vacuum jacketed model packed with .09" x .175" x .175" S.S. Heli-Pak column internals. The column operated at both atmospheric and subatmospheric pressures at a 5:1 reflux ratio.

In order to perform the high temperature segment of the characterization, the liquid was transferred to a modified Hempel apparatus. This consisted simply of a round bottom distillation flask with thermowell, a liquid dividing still head with warm and cold condensing water capability, product receiver, tilting McLeod manometer and vapor trap. The system was evacuated with a Welch brand mechanically backed diffusion pump.

#### EXPERIMENTAL

A five gallon sample was removed from Paraho above-ground oil drum #52-SH-08-01 in the manner prescribed under the contract. That is, the 55 gallon drum was heated for two hours on the high setting of a band-type drum heater wrapped around the lower third of the drum. The drum was then agitated vigorously for approximately one minute and a sample withdrawn through a spigot on the drum cap. No filtration was performed.

About one gallon of the oil sample was then dewatered by centrifugation at 140°F. Samples of the raw dewatered crude were submitted for analytical work-up and the

remainder of the oil was charged to a 30mm x 48" Podbielniak fractionating column. Raw crude oil data is shown in Table II-1.

The Podbielniak still was operated at a 5:1 reflux ratio to collect fractions in 100°F increments from the IBP up to 600°F. Both volume and weight measurements of the charge and product were made.

The >600°F residue was transmitted to the Synthetic Oils lab where it was subjected to further fractionation. Equipment limitations precluded fractionation beyond the 600°F limit on the Podbielniak unit without fear of thermal decomposition. An alternate method was devised for this high temperature fractionation by distilling at low pressures (<1mm Hg) and total product take-off on the modified Hempel apparatus described previously. The material was fractionated again in 100°F increments above the 600°F initial point to the temperature at which thermal decomposition was observed. Once again, both weight and volume measurements of the charge and product fractions were made.

Samples of each discrete fraction were subjected to analysis as shown in Table II-2.

#### EXPERIMENTAL RESULTS

Raw analytical results are shown in Table II-2. Fractionation documentation can be found in Figure II-1. The variation of API gravity and contents of sulfur, arsenic, nitrogen and basic nitrogen by boiling fractions are documented in Figures II-2 through II-6.

TABLE II-1

## CRUDE SHALE OIL EVALUATION

SAMPLE TYPE: PARAHO ABOVE - GROUND

SAMPLE NUMBER: 52 - SH - 08 - 01

ITEM		ITEM	
CARBON, WT %	84.94	GRAVITY, °API	20.9
HYDROGEN, WT %	11.43	SPECIFIC GRAVITY	0.9285
NITROGEN, WT %	1.97	VIS at 100°F, SU	43.4
SULFUR, WT %	.62	VIS at 140°F, SU	81.3
OXYGEN, WT %	1.04	K FACTOR	11.4
BASIC NITROGEN, WT %	1.48	REID VAPOR PRESSURE	0.2
PHENOLS, WT %	0.899	DISSOLVED H <sub>2</sub> S, ppm	33
IRON, ppm	66	RAMSBOTTOM CARBON	1.62
NICKEL, ppm	5	SALT, #/1000 bbl	1.98
VANADIUM, ppm	<1	BS & W, Vol %	TRACE
ARSENIC, ppm	35	ACID NUMBER	1.90
ORGANIC CHLORIDE, ppm	13	POUR POINT, °F	70
COLOR	8+	MALEIC ANHYDRIDE VALUE	82
RECOVERY ON DEWATERING, Vol %	99.6		

TABLE II-2

## CRUDE SHALE OIL EVALUATION

SAMPLE TYPE:

PARAHO ABOVE-GROUND

SAMPLE NUMBER: 52-SH-08-01

ITEM / FRACTION	(275)- 300	300- 400	400- 500	500- 600	600+	600- 700	700- 800	800+
Yield, LV %	1.4	4.1	9.7	12.9	71.2	12.9	9.2	49.1
Yield, Wt %	1.2	3.6	8.9	12.3	73.1	13.7	9.7	49.6
K Factor	-	11.2	11.2	11.2	11.4	11.4	11.5	-
API Gravity	48.8	41.4	34.1	28.3	16.8	22.4	20.6	14.9
Specific Gravity	0.7848	0.8184	0.8545	0.8855	0.9541	0.9194	0.9303	0.9665
Carbon, Wt %	86.16	-	81.33	85.36	85.3	84.5	85.6	84.3
Hydrogen, Wt %	12.01	12.5	12.3	11.9	11.3	11.8	10.8	10.6
Nitrogen, Wt %	0.57	1.67	1.92	2.46	2.25	1.86	1.74	2.45
Basic Nitrogen, Wt %	0.15	0.87	0.99	0.90	1.31	1.17	1.20	1.37
Sulfur, Wt %	0.98	1.08	0.88	0.84	0.61	0.68	0.64	0.58
Phenols, Wt %	-	5.3	3.6	-	-	-	-	-
Iron, ppm	-	-	-	-	-	1	<1	138
Nickel, ppm	-	-	-	-	-	<1	<1	10
Vanadium, ppm	-	-	-	-	-	2	<1	2
Arsenic, ppm	-	28	50	10	-	16	19	32
Ramsbottom Carbon	-	-	-	-	-	-	-	-
Saturates, Vol %	-	-	-	-	-	0.41	0.35	4.02
Olefins, Vol %	-	-	-	-	-	43.0	48.5	61.2
Aromatics, Vol %	-	-	-	-	-	-	-	-
Pour Point, °F	-	-	-	-	-	57.0	51.5	38.8
Viscosity, 100°F, cst	-	1.2	2.29	5.60	83.2	20.8	55.68	-
Viscosity, 140°F, cst	-	0.67	1.04	1.63	-	-	-	-
Viscosity, 210°F, cst	-	-	-	-	16.88	3.43	5.81	-

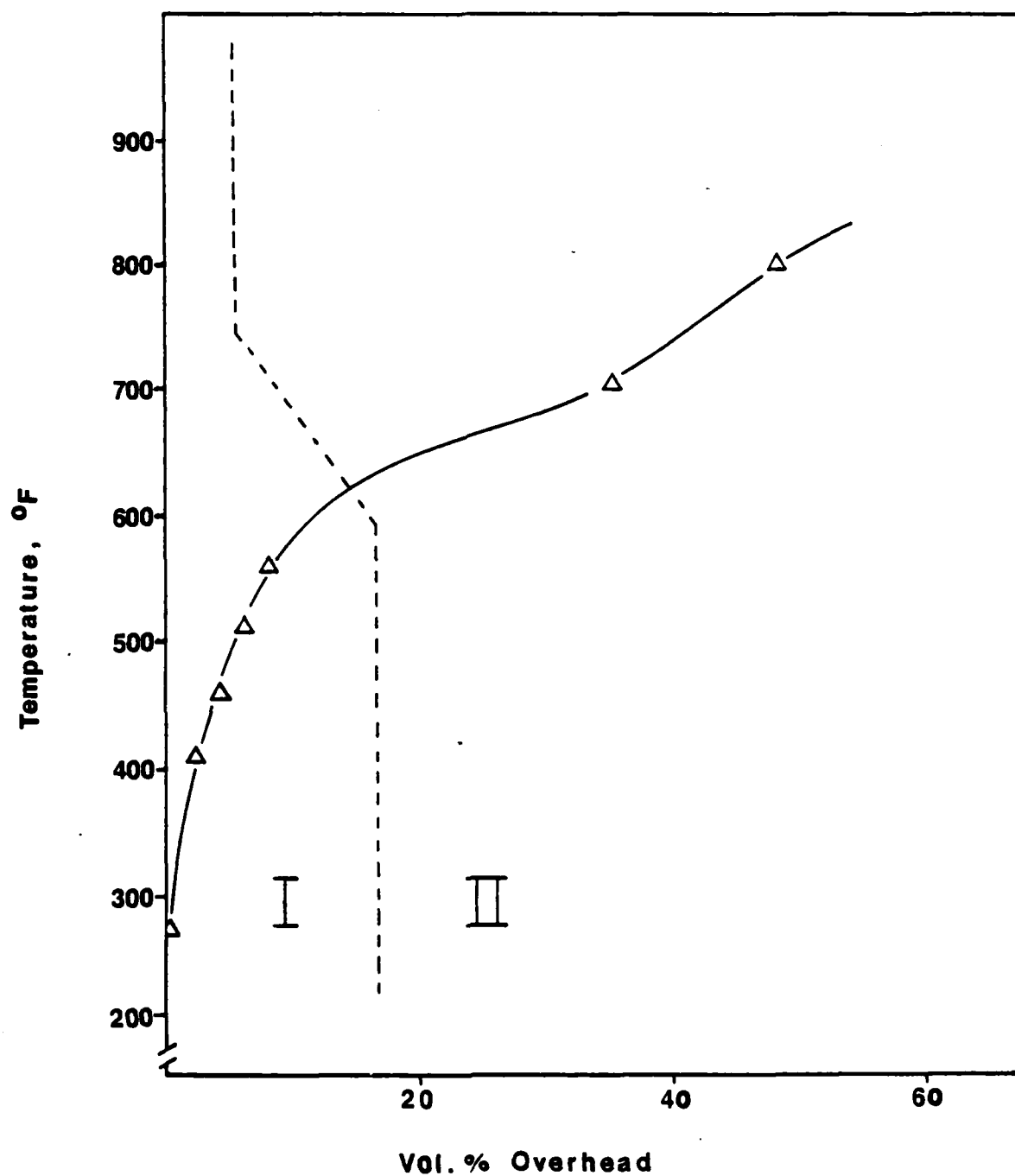


Figure II-1. Podbielniak (I) And Hempel (II)  
Fractionation Of Paraho Crude Shale Oil

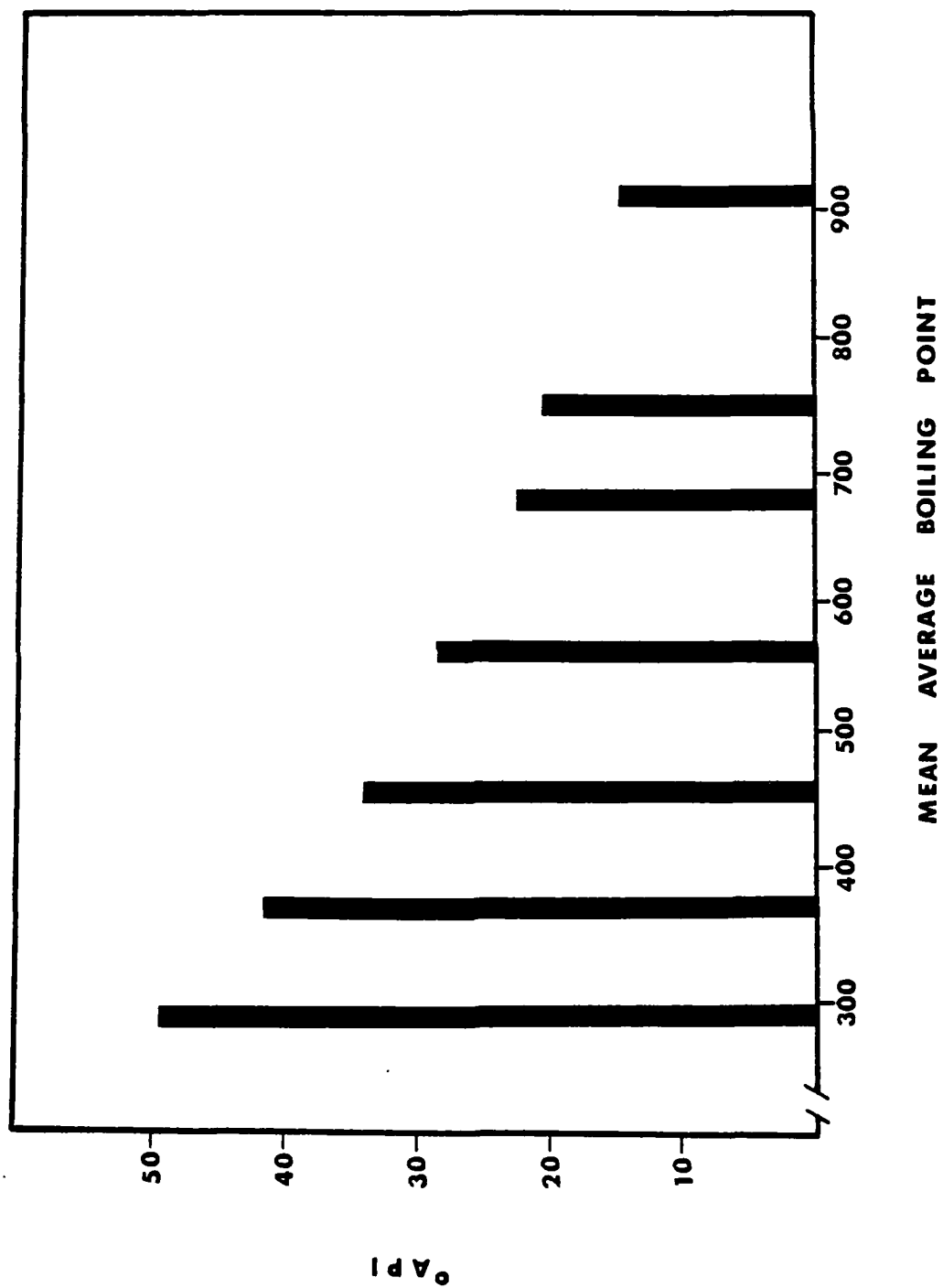


Figure 11-2. API Gravity As A Function Of Boiling Range  
For Crude Paraho Shale Oil



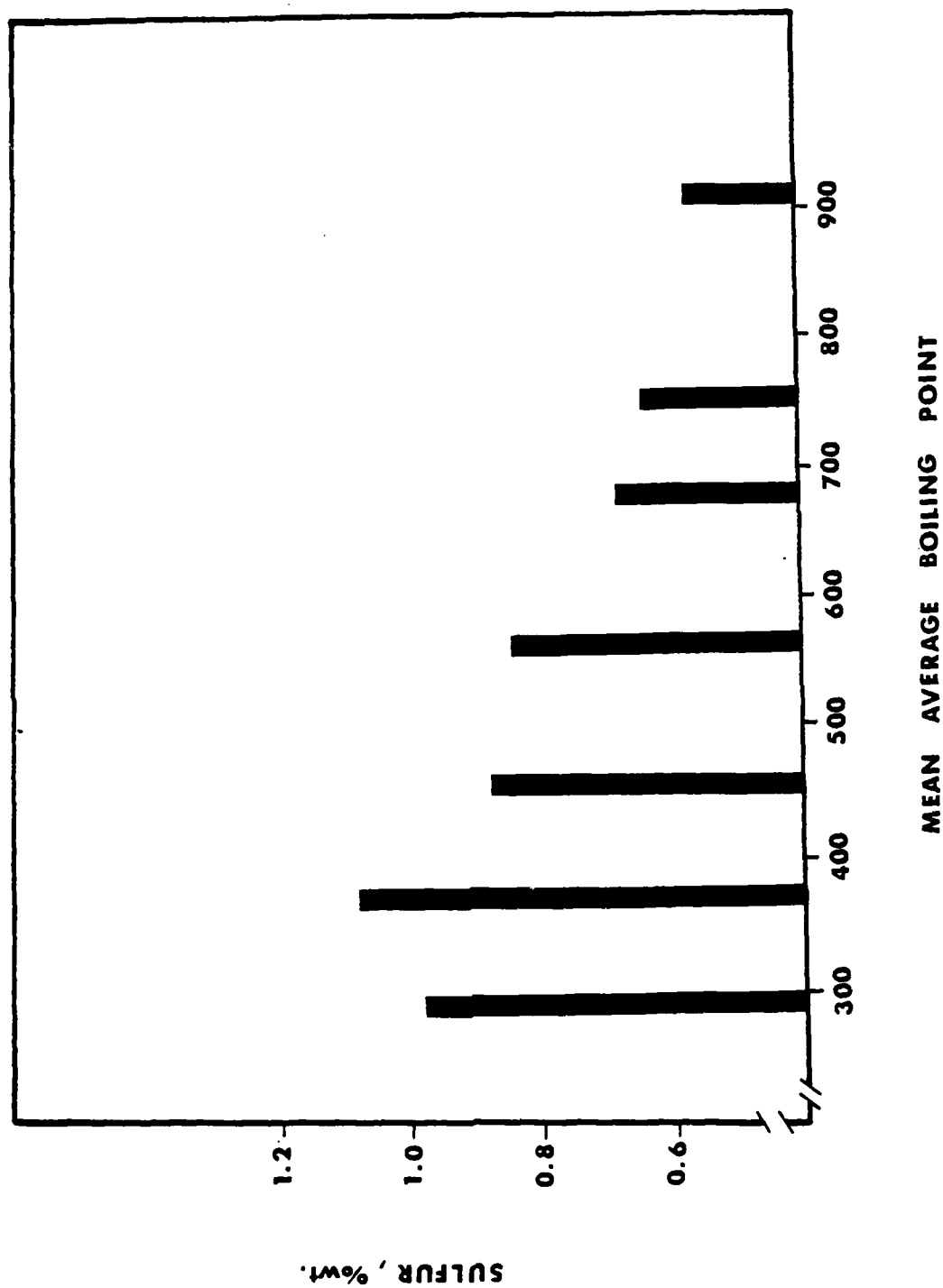


Figure II-3. Sulfur Content As A Function Of Boiling Range For Crude Paraho Shale Oil

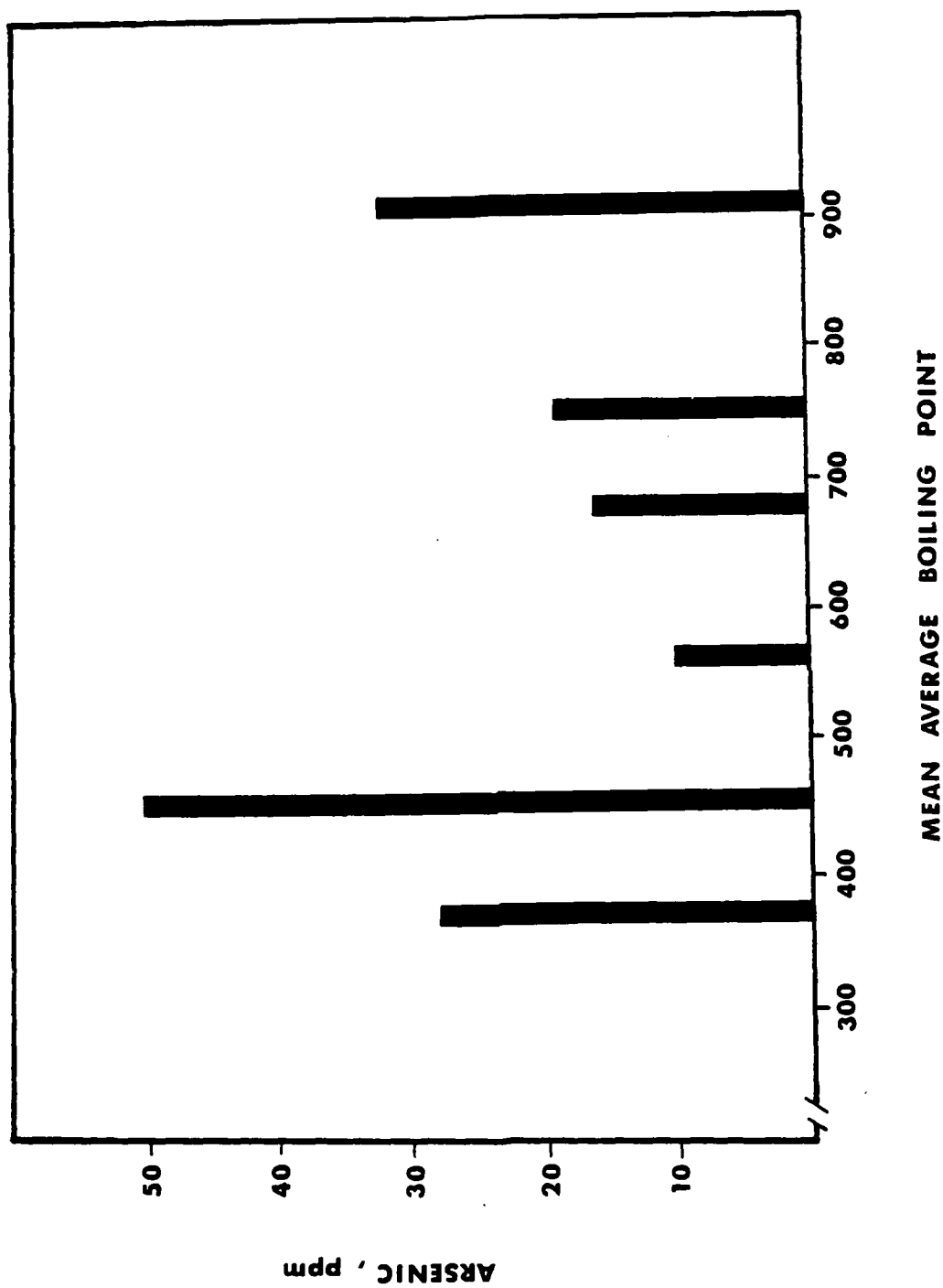


Figure II-4. Arsenic Content As A Function Of Boiling Range For Crude Paraho Shale Oil

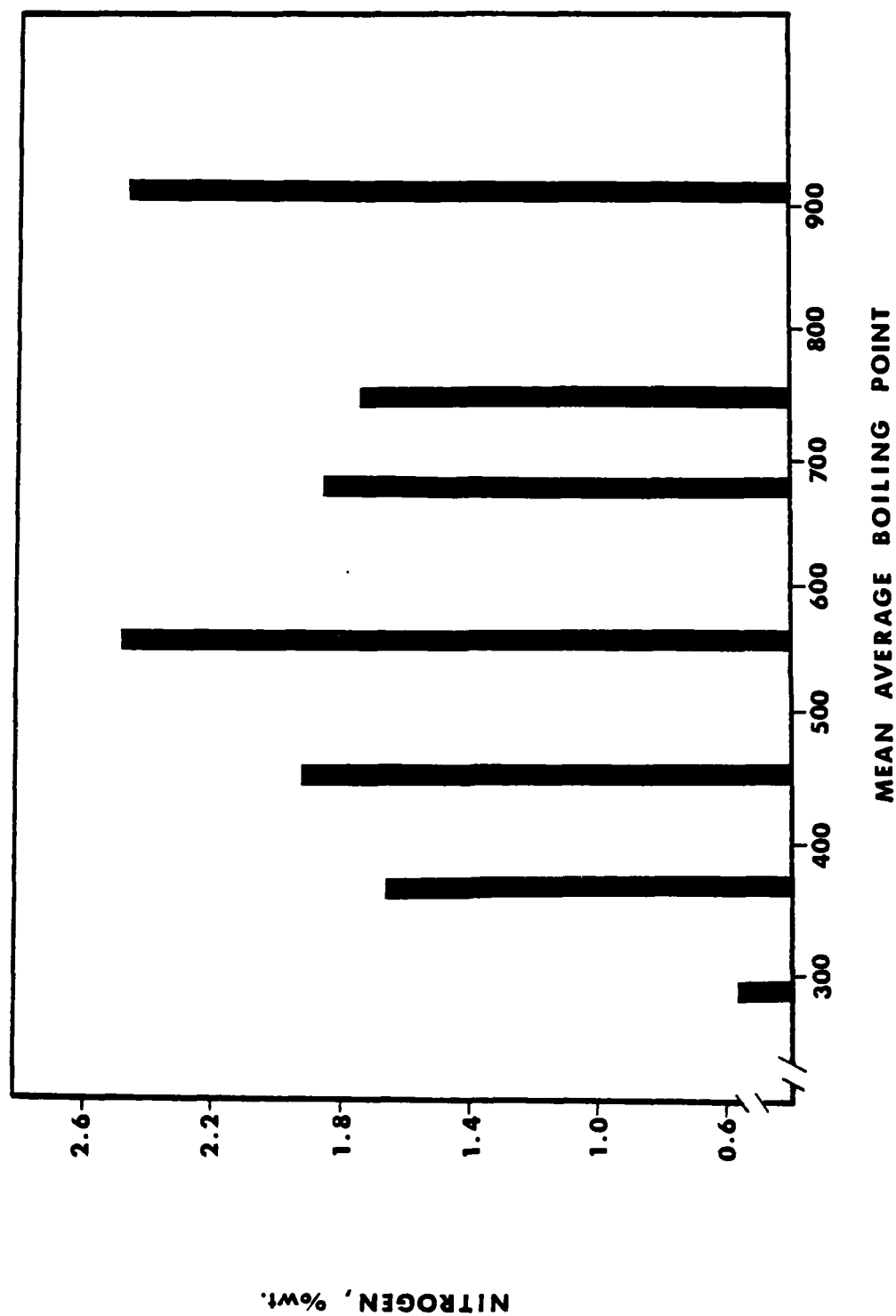


Figure II-5. Nitrogen Content As A Function Of Boiling Range For Crude Paraho Shale Oil

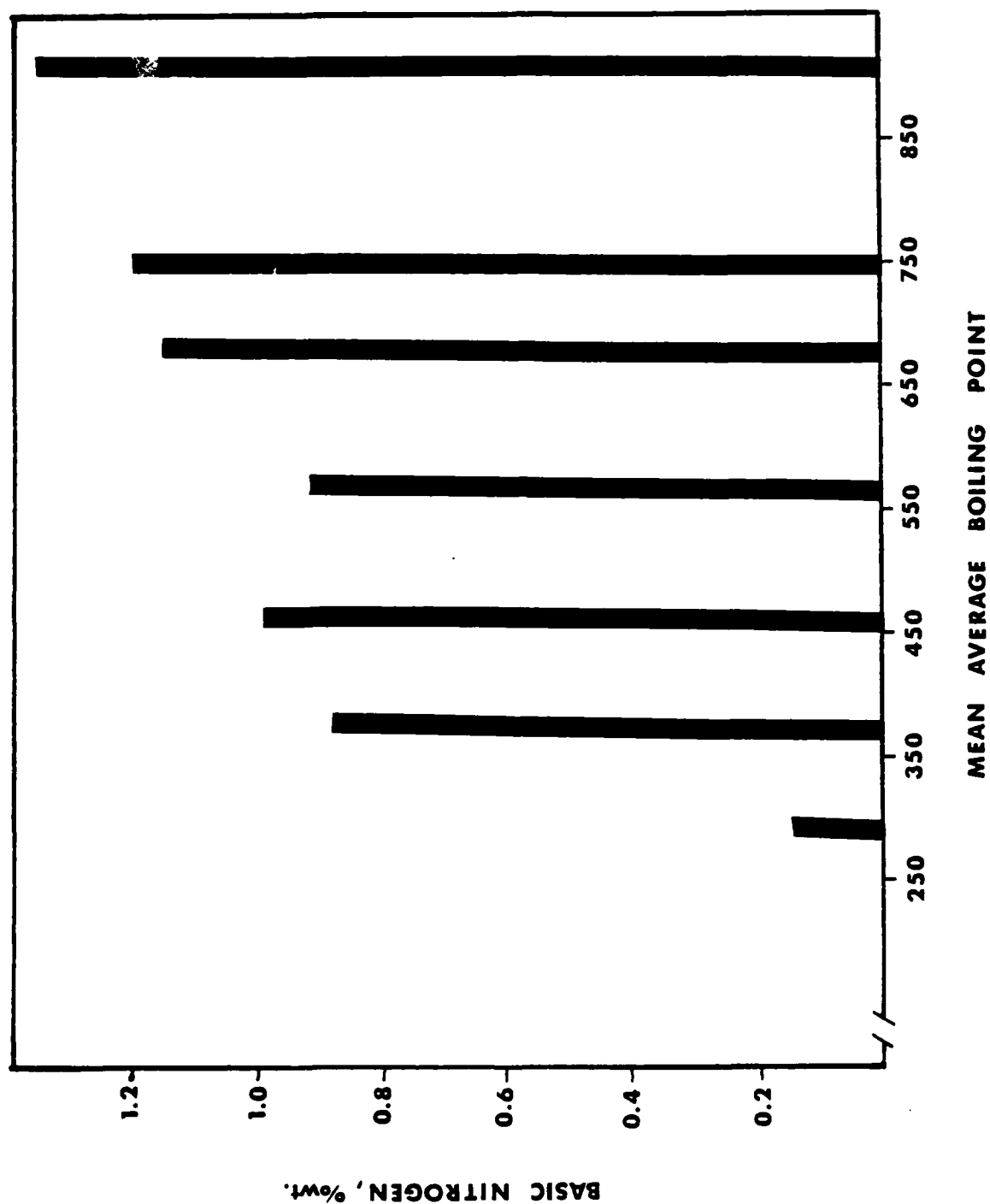


Figure II-6. Basic Nitrogen Content As A Function Of Boiling Range For Crude Paraho Shale Oil

## DISCUSSION

Boiling ranges quoted for the fractions above 600°F are nominal ranges. This is due mainly to the fractionating efficiency sacrificed with the previously described apparatus in order to maintain low system pressures and temperatures, as well as short column residence time to avoid thermal cracking.

While the majority of the analytical functions were performed within the Research Department, some analyses were performed by independent analysts due to internal equipment limitations. Quantities of certain distillate fractions produced limited the number of analyses which could be performed on those fractions (e.g., IBP-300°F, 300-400°F).

The Watson characterization factor, K, for each of the fractions was derived from correlations of viscosity and API gravity.

## CONCLUSIONS

The Paraho crude oil has been successfully separated into the nominal boiling ranges shown in Table II-2. The most noteworthy obstacle was the avoidance of thermal cracking, a phenomenon observed at lower temperatures for shale oils than for most petroleum crudes.

SECTION III  
CRUDE SHALE OIL HYDROTREATER

The crude shale hydrotreater provided for the EXTRACT-ACRACKING process supplies the following functions:

1. Desulfurization
2. Demetallization, and in particular, dearsenation
3. Olefin saturation
4. Denitrogenation
5. Deoxygenation

In contrast to most work in this field, this crude shale hydrotreater is intended to be a low severity, low hydrogen consumption unit. It provides feedstock cleanup with respect to items 1 to 3, with as little denitrogenation as possible. The combination of low hydrogen addition, while removing metallic contaminants and olefins for handling purposes, is projected to provide an ideal combination of feedstock preparation for both extraction and fluid catalytic cracking.

Work in this area was of necessity extensive, particularly for preparation of samples for further processing. The studies performed were:

1. Parameter screening studies, including operating severity and catalyst.
2. Sample preparation, catalyst stability studies.
3. Extended sample preparation and catalyst aging studies.

These studies ranged from 16 hour tests for the parameter screening studies to over 700 hours for the aging tests.

# 1. PARAMETER VARIATION STUDIES

## SUMMARY

Full range above-ground retorted shale oil was hydro-treated over cobalt molybdate, as well as nickel molybdate catalyst, in order to quickly screen the response of the crude shale hydrotreater to Paraho oil feed. Temperatures were varied between 650 and 750°F, pressures from 1000 to 2000 psig, and liquid hourly space velocity from 1 to 4 hr<sup>-1</sup>. Hydrogen circulation was maintained at 4000 SCFB.

Each experimental run was assigned a four digit code generated in the form:

2XYZ

Where 2 signifies the Paraho oil feed,

X = 1 for Co/Mo catalyst

2 for Ni/Mo catalyst

Y = 1 for 1000 psig pressure

2 for 1500 psig pressure

3 for 2000 psig pressure

Z = specific material balance period

## OBJECTIVE

Parameter variation hydrotreating experiments were conducted with Paraho oil in order to rapidly prescreen

this oil's response to multiple operating variables. A higher range of pressures was chosen than for the Occidental experiments since higher severity treatment was predicted in order to meet crude shale hydrotreater module objectives.

#### MECHANICAL DESCRIPTION

The nominal 1" I.D. universal trickle flow reactor described previously in Volume II was utilized. No pre-purification of the feed was practiced and no guardbeds were in service during the three sets of parameter variation experiments.

An 80-ml sample of each material balance product was stripped at 300 to 350°F for three to five hours, after which the API gravity, sulfur and nitrogen content were measured.

#### CHEMICAL/CATALYST DESCRIPTION

In each of the three experimental series, the reactor was packed with a 100-ml void filled bed of 1/16" extruded catalyst which was subsequently presulfided using H<sub>2</sub>S. Both cobalt molybdate and nickel molybdate catalyst types were investigated. Void filling was accomplished with Ottawa sand mixed in equal quantities with catalyst.

The Paraho shale feed was drawn from drum #52-SH-06-01 obtained in the original crude shale supply from the Air Force. Properties of the oil used for material balance purposes are shown in Table III-1.



TABLE III-1

PARAHO ABOVE-GROUND RETORTED  
SHALE OIL PROPERTIES

GRAVITY, °API	21.7
SULFUR, WT. %	0.63
NITROGEN, WT. %	1.98
OXYGEN, WT. %	1.04(1)

(1) No oxygen analysis for Drum #52-SH-06-01.  
Oxygen value taken from similar Drum  
#52-SH-07-01.

## EXPERIMENTAL PROCEDURE

The procedure for each separate study, designated PV-1, PV-2 and PV-3, will be explained individually.

PV-1 Experimental - The 1" I.D. universal reactor was packed with tabular alumina, followed by a 100-ml cobalt molybdate catalyst bed (void filled with 100-ml of Ottawa sand), and a preheat section of tabular alumina. The unit was pressure tested with nitrogen and hydrogen to 1700 psig and then was presulfided with  $H_2S$  at gradually increasing temperatures until holding at 800°F for one hour.

Material balance periods of eight hours' duration were in effect. No product fractionations were performed, but an 80-ml sample of each test period was stripped and analyzed.

The experimental sequence and test conditions are shown in Table III-2.

PV-2 Experimental - The reactor was packed with tabular alumina, followed by a 100-ml cobalt molybdate catalyst bed (void filled with 100-ml Ottawa sand), and finally a preheat section of tabular alumina. The unit was pressure-checked with nitrogen and hydrogen to 2200 psig and was presulfided with  $H_2S$  as in PV-1.

Eight hour material balance periods were in effect. No product fractionations were performed, but an 80-ml sample of each test period was stripped and analyzed.

TABLE III-2

EXPERIMENTAL SEQUENCE AND  
CONDITIONS - PARAHO CRUDE SHALE  
PARAMETER VARIATIONS HYDROTREATMENT

<u>PV #</u>	<u>SAMPLE #</u>	<u>TEMP., °F</u>	<u>PRESS., PSIG</u>	<u>LHSV</u>	<u>CATALYST</u>
PV-1	2111	650	1000	2	Co Mo
	2112	700	1000	2	"
	2113	700	1000	4	"
	2114	700	1000	1	"
	2115	750	1000	2	"
	2121	750	1500	2	"
PV-2	2122	650	1500	2	"
	2131	650	2000	2	"
	2132	700	2000	2	"
	2133	700	2000	4	"
	2134	700	2000	1	"
	2135	750	2000	2	"
PV-3	2211	650	1000	2	Ni Mo
	2221	700	1500	2	"
	2222	700	1500	1	"
	2223	700	1500	4	"
	2231	700	2000	2	"
	2232	750	2000	2	"

The experimental sequence and test conditions are shown in Table III-2.

PV-3 Experimental - The reactor was packed with tabular alumina, followed by a 100-ml nickel molybdate catalyst bed (void filled with 100-ml of Ottawa sand), and a preheat alumina section. The unit was pressure checked with nitrogen and hydrogen to 2200 psig, then was presulfided with  $H_2S$  as in PV-1.

Eight hour material balance periods were utilized. No product fractionations were performed, but an 80-ml sample of each material balance was stripped and analyzed.

The experimental sequence and test conditions are shown in Table III-2.

## RESULTS

Data summaries and raw results can be found in Tables III-3 through III-5 and Figures III-1 through III-7.

## DISCUSSION/CONCLUSIONS

Differing severity requirements for sulfur and nitrogen removal are shown graphically in Figures III-1 and III-2. At 1000 psig pressure, desulfurization demonstrated an apparent reaction initiation requirement of about 635°F, while nitrogen required on the order of 650°F. Increasing the system pressure to 2000 psig significantly increased both the rates of desulfurization and denitrogenation, as well as reducing the apparent reaction initiation temperature requirements.

TABLE III-3

## CRUDE SHALE OIL HYDROTREATING SERIES PV-1

Period	2111	2112	2113	2114	2115	2121
<b>OPERATING CONDITIONS</b>						
Temperature, °F	650	699	699	699	750	750
Pressure, PSIG	998	1015	1005	1014	1024	1500
LHSV, Hr <sup>-1</sup>	1.78	1.85	3.68	0.97	1.75	1.92
H <sub>2</sub> Rate, SCFB	4501	4338	4413	4235	4676	4226
<b>MATERIAL BALANCE</b>						
Weight Percent of Feed						
Feed	100	100	100	100	100	100
H <sub>2</sub> In	7.34	7.08	7.20	6.91	7.63	6.90
Subtotal In	107.34	107.08	107.20	106.91	107.63	106.90
H <sub>2</sub> O	(0.69)	0.87	0.80	(0.97)	(1.11)	(1.11)
NH <sub>3</sub>	-	(0.05)	(0.19)	(0.78)	(0.70)	(1.21)
H <sub>2</sub> S	(0.54)	(0.62)	(0.58)	(0.66)	(0.66)	(0.67)
H <sub>2</sub> Out	*-	5.24	6.35	4.64	6.05	5.30
C <sub>1</sub>	-	0.20	0.15	0.14	0.58	0.57
C <sub>2</sub>	-	0.36	0.26	0.30	0.04	0.31
C <sub>3</sub>	-	0.32	0.23	0.28	0.03	0.24
C <sub>4</sub>	-	0.23	0.15	0.16	0.02	0.13
C <sub>5</sub>	-	-	0.11	0.18	0.03	0.25
Stabilized Liquid	90.63	99.51	101.53	96.86	97.58	98.08
Subtotal	-	107.40	110.34	104.98	106.79	107.86
Closure	-	100.3	102.9	98.2	99.2	100.9
Hydrogen Consumption, SCFB	-	1125	520	1391	965	978
<b>PRODUCT PROPERTIES</b>						
°API	25.2	26.8	25.5	29.3	30.2	32.9
Sulfur, Wt %	0.13	0.0451	0.0845	0.0086	0.0081	0.0032
Nitrogen, Wt %	(1.98)	(1.95)	(1.80)	(1.38)	(1.44)	(1.00)
Oxygen, Wt %	-	-	-	-	-	-

( ) CALCULATED

\* NO OFFGAS ANALYSIS PERFORMED

TABLE III-4

## CRUDE SHALE OIL HYDROTREATING SERIES PV-2

Period	2 1 2 2	2 1 3 1	2 1 3 2	2 1 3 3	2 1 3 4	2 1 3 5
<b>OPERATING CONDITIONS</b>						
Temperature, °F	654	647	705	707	703	754
Pressure, PSIG	1506	1999	1994	2001	1981	1997
LHSV, Hr <sup>-1</sup>	1.59	1.67	1.83	3.85	1.05	1.94
H <sub>2</sub> Rate, SCFB	5121	4822	4460	4161	3905	4100
<b>MATERIAL BALANCE</b>						
Weight Percent of Feed						
Feed	100	100	100	100	100	100
H <sub>2</sub> In	8.36	7.87	7.28	6.79	6.37	6.69
Subtotal In	108.36	107.87	107.28	107.79	106.37	106.69
H <sub>2</sub> O	(0.80)	(0.85)	(1.05)	(0.69)	(1.17)	(1.17)
NH <sub>3</sub>	(0.14)	(0.54)	(1.36)	-	(1.28)	(1.78)
H <sub>2</sub> S	(0.57)	(0.61)	(0.66)	(0.64)	(0.65)	(0.66)
H <sub>2</sub> Out	6.33	5.66	3.82	4.92	3.73	4.16
C <sub>1</sub>	-	0.16	-	0.41	0.30	-
C <sub>2</sub>	1.06	0.19	0.80	0.49	0.48	0.16
C <sub>3</sub>	1.59	0.11	0.52	0.32	0.30	0.11
C <sub>4</sub>	2.44	0.07	0.30	0.15	0.11	0.05
C <sub>5</sub>	1.00	0.02	1.35	0.87	1.28	0.09
Stabilized Liquid	96.50	98.44	92.55	96.95	96.50	93.02
Subtotal	110.43	106.64	102.41	105.50	105.80	101.20
Closure	101.9	98.9	95.5	98.8	99.5	94.9
Hydrogen Consumption, SCFB	1239	1351	2122	1146	1621	1548
<b>PRODUCT PROPERTIES</b>						
°API	26.7	28.0	31.6	31.1	31.3	34.8
Sulfur, Wt %	0.10	0.0613	0.0045	0.0291	0.0148	0.0054
Nitrogen, Wt %	(1.93)	(1.56)	(0.93)	(1.98)	(0.96)	(0.55)
Oxygen, Wt %	-	-	-	-	-	-

( ) Calculated

TABLE III-5

## CRUDE SHALE OIL HYDROTREATING      SERIES PV-3

Period	2211	2221	2222	2223	2231	2232
<b>OPERATING CONDITIONS</b>						
Temperature, °F	650	700	700	700	700	750
Pressure, PSIG	1012	1509	1496	1500	2003	1993
LHSV, Hr <sup>-1</sup>	1.94	2.04	0.99	3.30	2.28	1.88
H <sub>2</sub> Rate, SCFB	4147	3738	4060	4883	3527	4273
<b>MATERIAL BALANCE</b>						
Weight Percent of Feed						
Feed	100	100	100	100	100	100
H <sub>2</sub> In	6.77	6.10	6.63	7.97	5.75	6.97
Subtotal In	106.77	106.10	106.63	107.97	105.75	106.97
H <sub>2</sub> O	(0.83)	(1.00)	(1.07)	(.93)	(1.17)	(1.17)
NH <sub>3</sub>	(0.63)	(0.98)	(1.66)	(0.23)	(0.62)	(1.83)
H <sub>2</sub> S	(0.51)	(0.63)	(0.65)	(0.49)	(0.58)	(0.67)
H <sub>2</sub> Out	5.93	4.35	4.57	7.47	5.15	4.44
C <sub>1</sub>	-	0.14	0.24	-	0.15	0.37
C <sub>2</sub>	0.08	0.76	1.49	0.46	0.42	0.90
C <sub>3</sub>	0.05	0.53	1.00	0.32	0.25	0.66
C <sub>4</sub>	0.02	0.29	0.55	0.20	0.14	0.33
C <sub>5</sub>	1.80	1.37	0.10	2.07	0.63	0.08
Stabilized Liquid	97.39	97.12	90.95	98.71	104.28	96.08
Subtotal	107.24	107.18	102.28	110.89	113.39	106.54
Closure	104.4	101.0	95.9	102.7	107.2	99.6
Hydrogen Consumption, SCFB	515	1072	1260	305	369	1548
<b>PRODUCT PROPERTIES</b>						
°API	25.6	29.5	33.8	25.7	28.4	34.9
Sulfur, Wt %	0.15	0.04	0.0159	0.17	0.0835	0.0011
Nitrogen, Wt %	(1.50)	(1.21)	(0.67)	(1.81)	(1.41)	(0.49)
Oxygen, Wt %	-	-	-	-	-	-

( ) Calculated

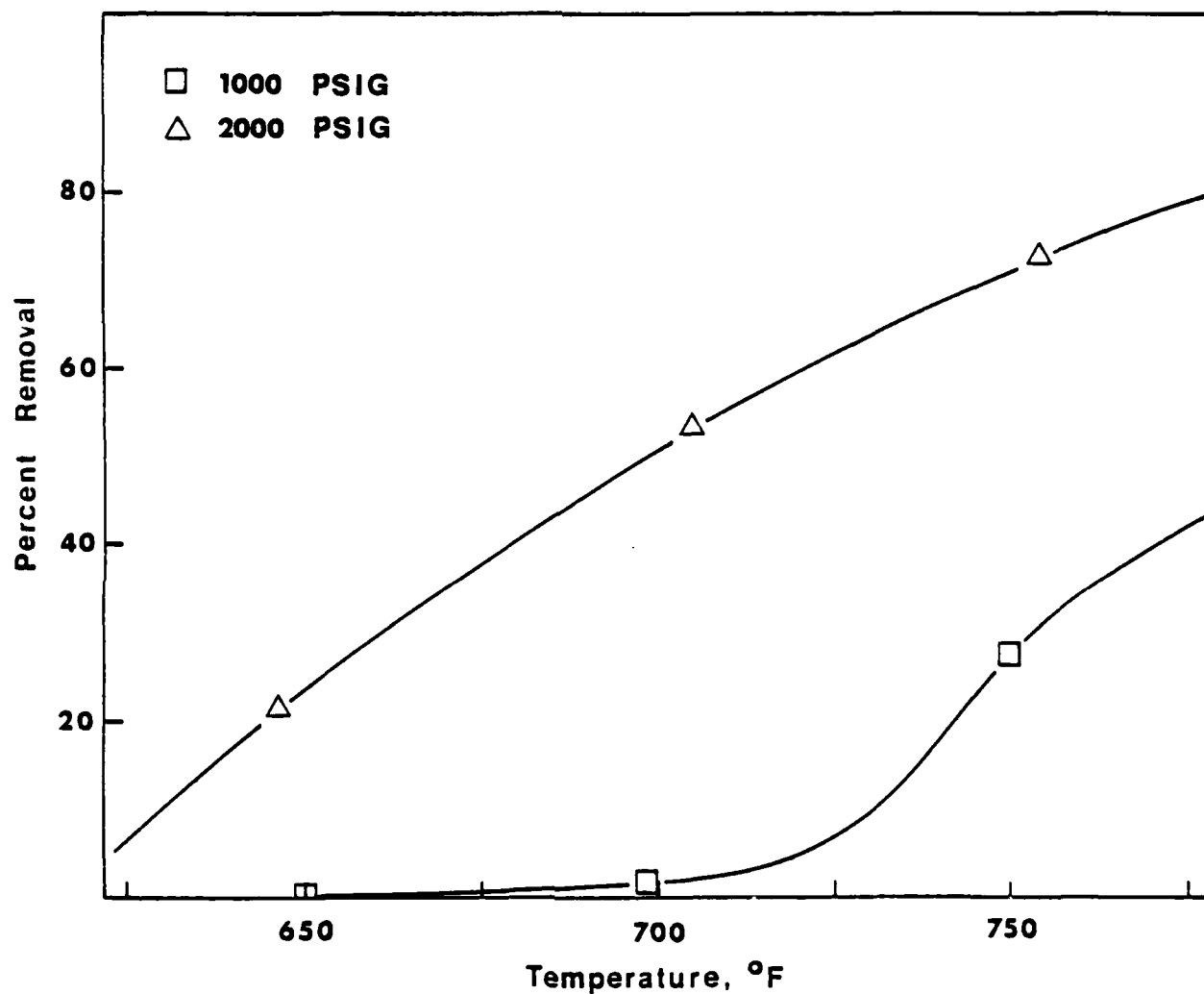


Figure III-1. Temperature Dependence Of Denitrogenation At 2 LHSV On Co/Mo



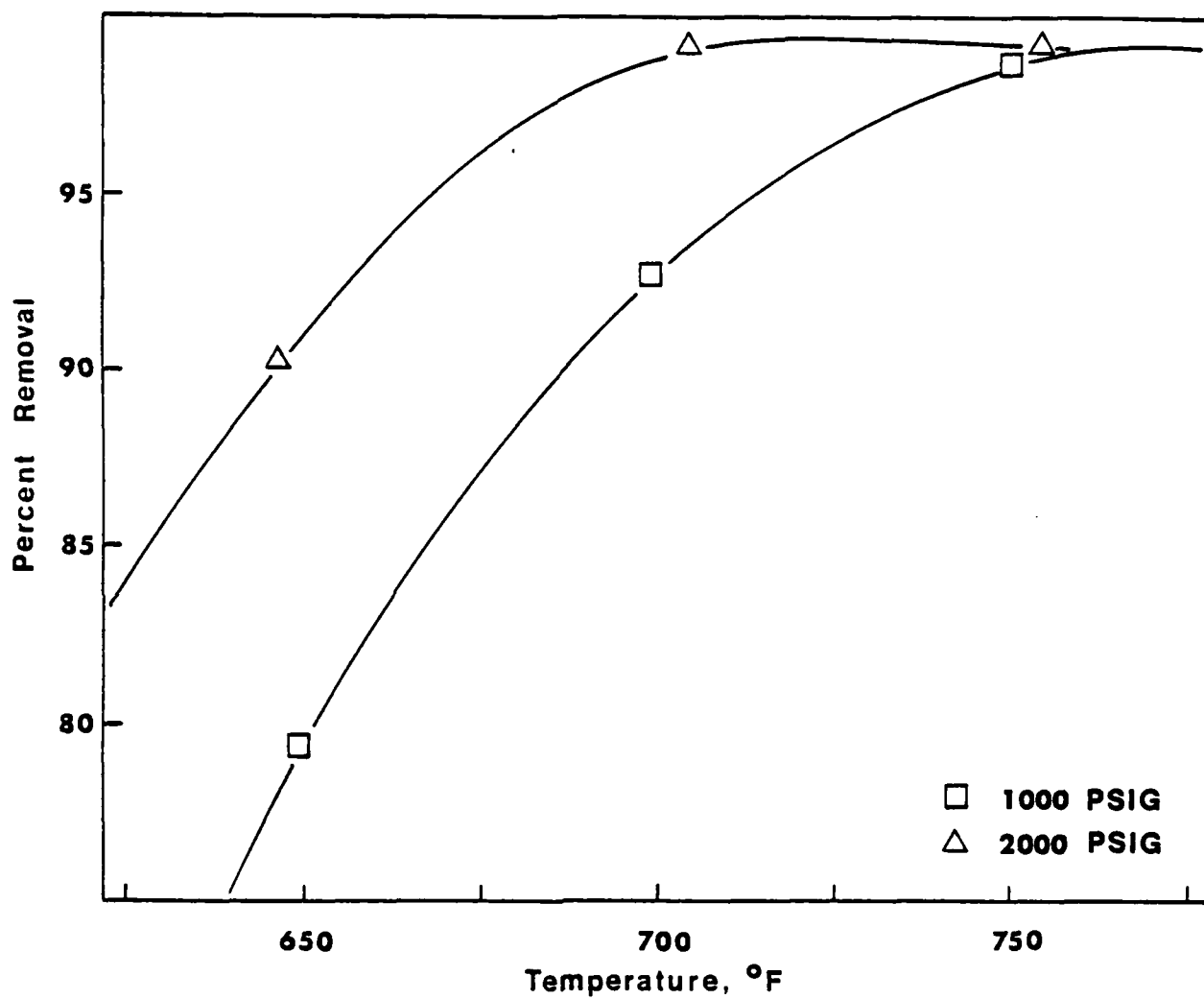


Figure III-2. Temperature Dependence Of Desulfurization At 2 LHSV On Co/Mo

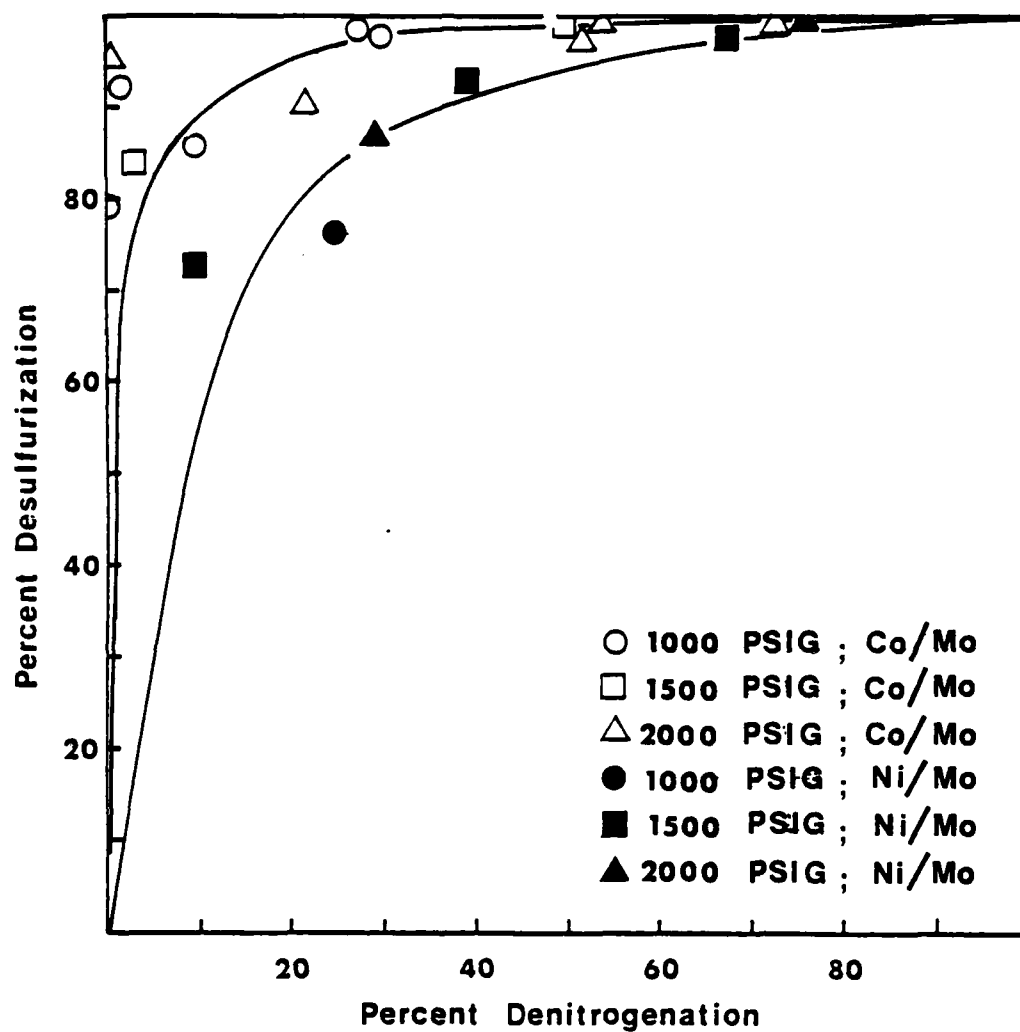


Figure III-3. Above-ground Shale Oil Hydrotreating

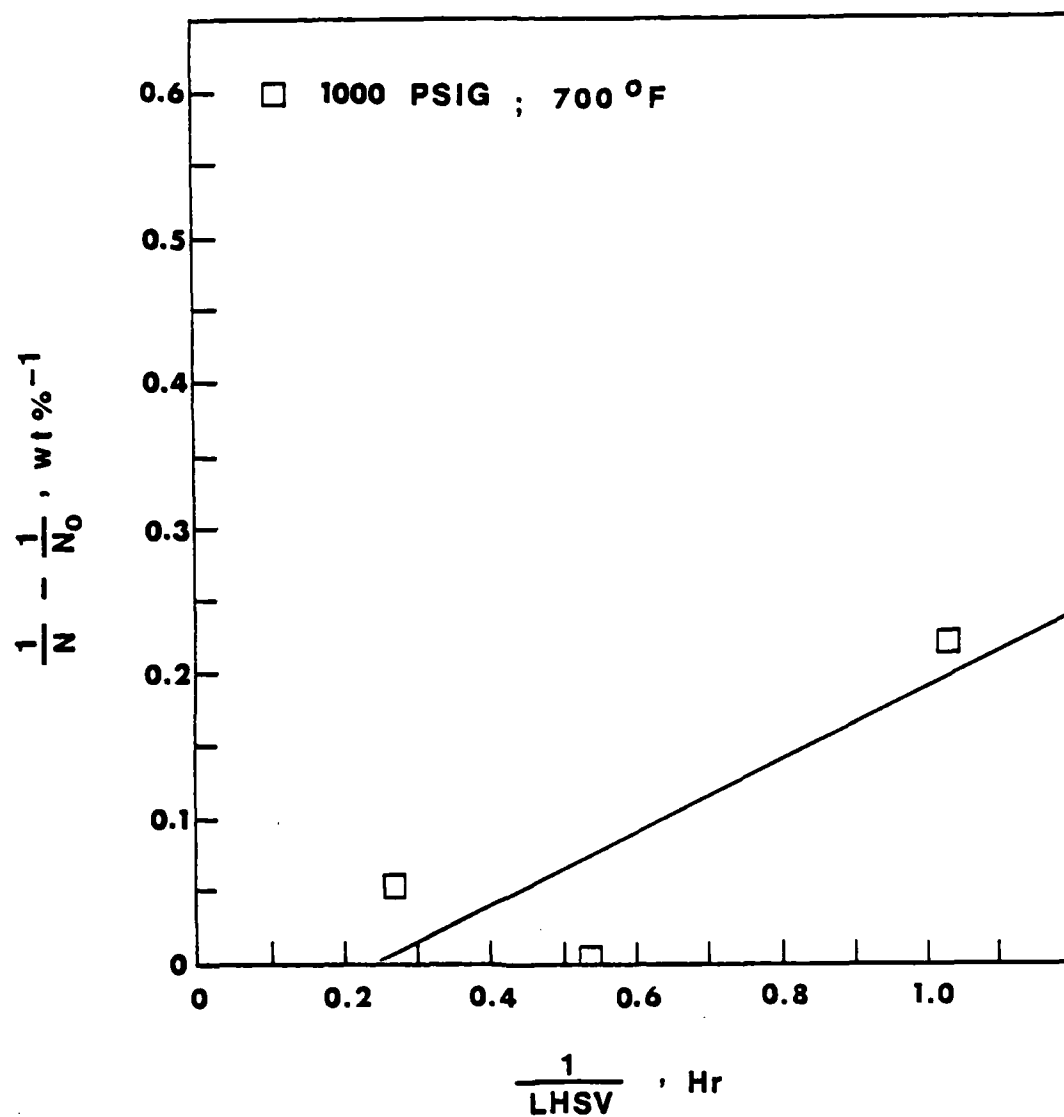


Figure III-4. Second-order Space Velocity Response Of Denitrogenation At 1000 PSIG Pressure Over Cobalt Molybdate Catalyst

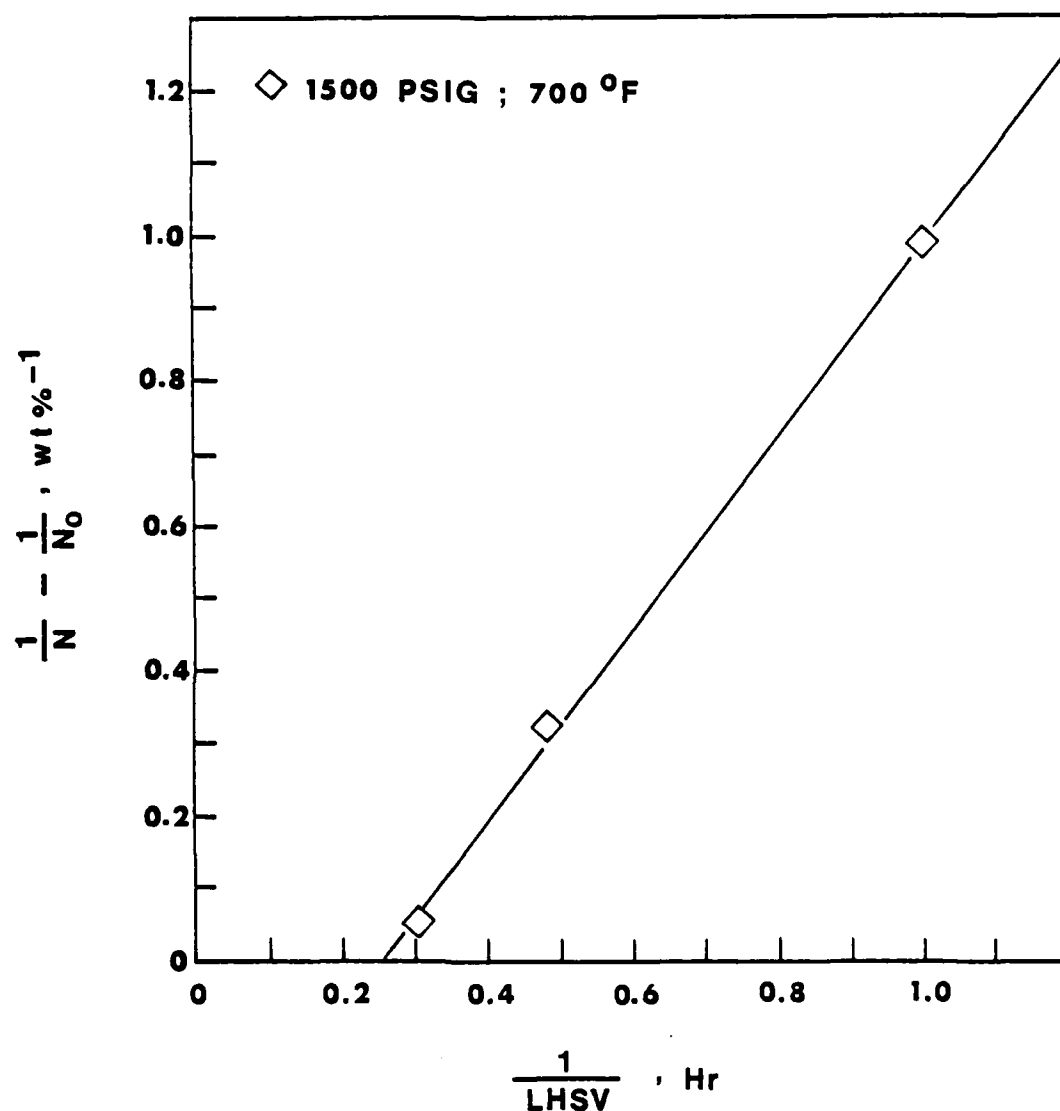


Figure III-5. Second-order Space Velocity Response Of Denitrogenation At 1500 PSIG Pressure Over Nickel Molybdate Catalyst

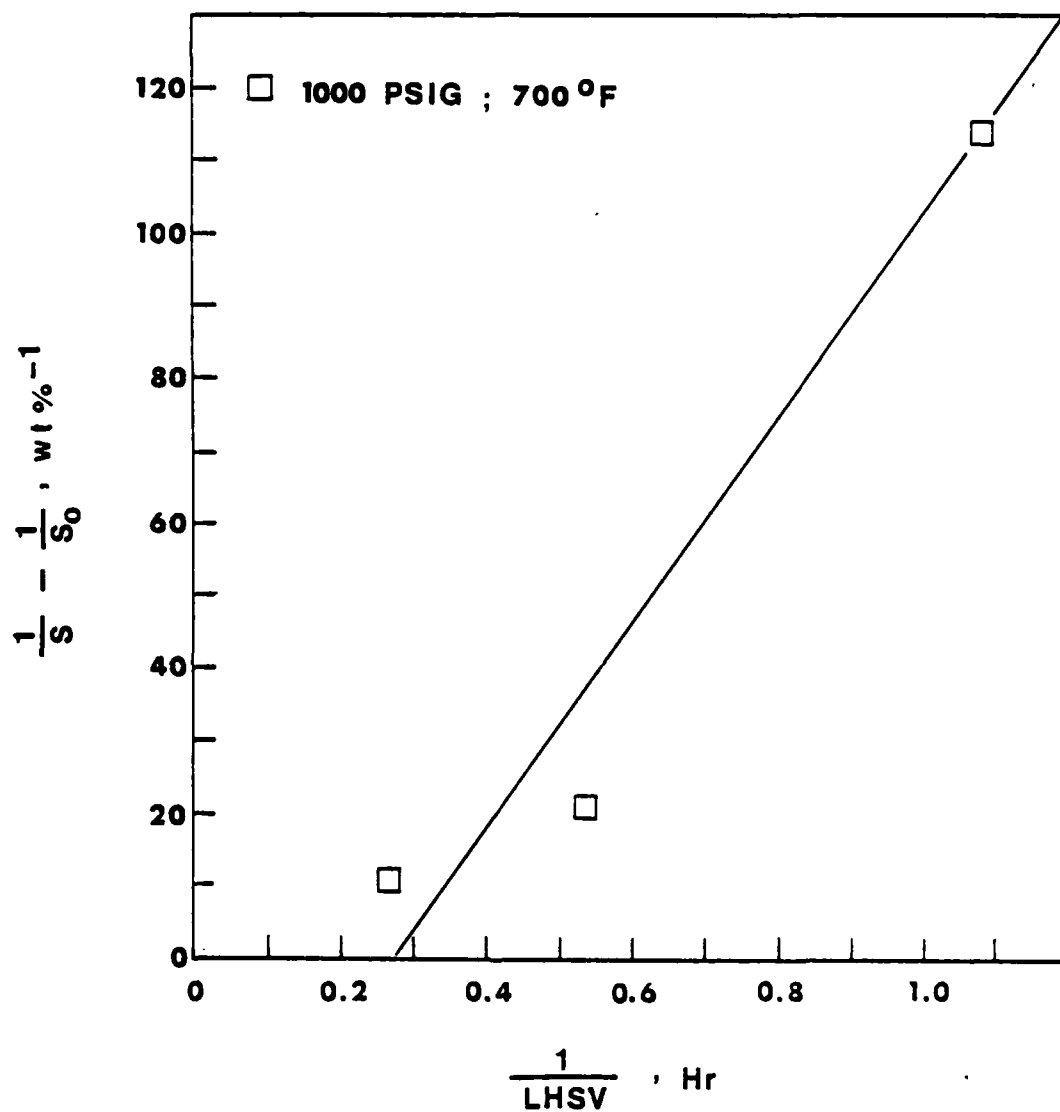


Figure III-6. Second-order Space Velocity Response Of Desulfurization At 1000 PSIG Pressure Over Cobalt Molybdate Catalyst

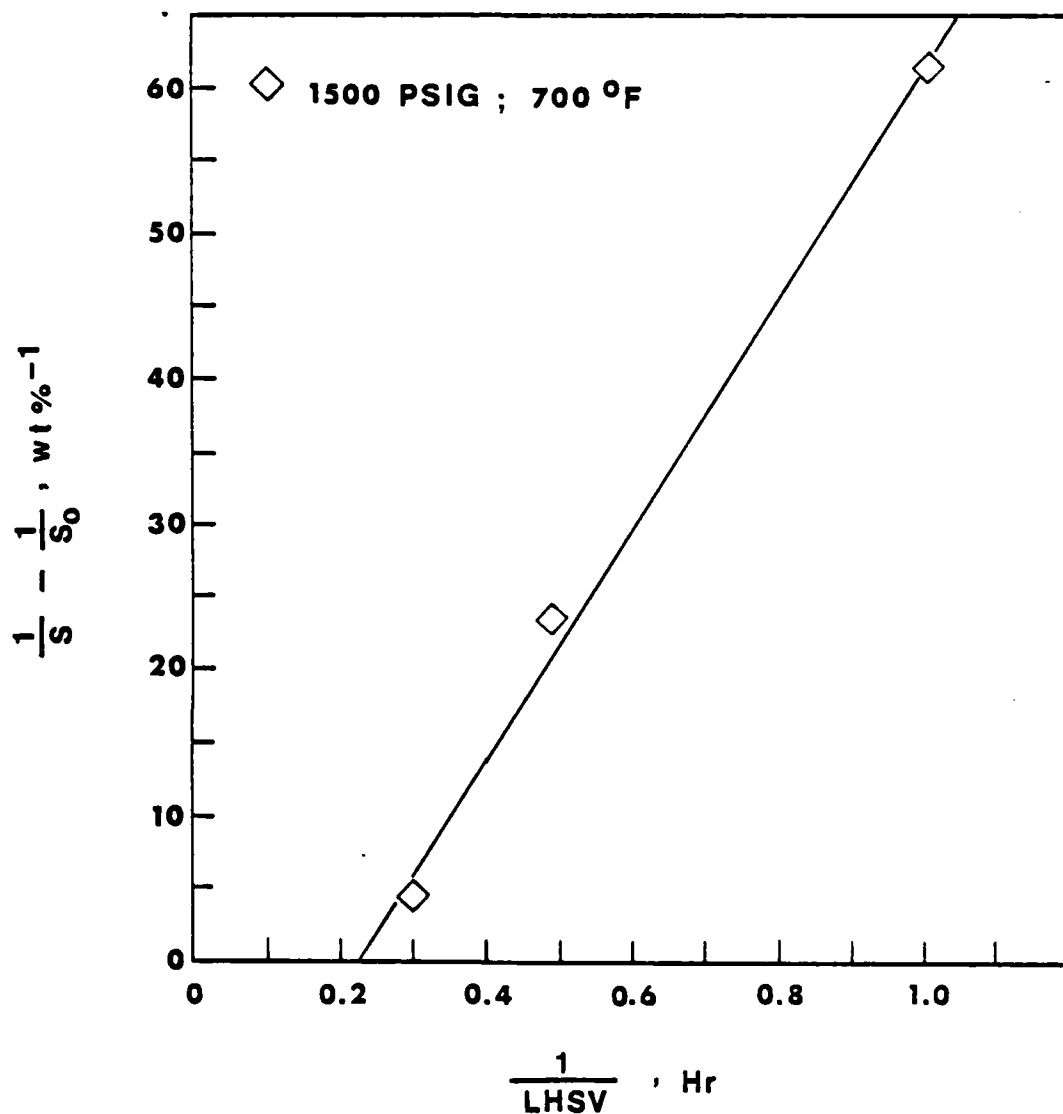


Figure III-7. Second-order Space Velocity Response Of Desulfurization At 1500 PSIG Pressure Over Nickel Molybdate Catalyst.

These relationships are also shown in Figure III-3. Desulfurizations as high as 80 percent were attained at no apparent denitrogenation. The expected relative desulfurization/denitrogenation relationships were also obtained when comparing the nickel and cobalt based catalysts with higher denitrogenations at equivalent desulfurizations attained with the nickel molybdate catalyst.

### CONCLUSIONS

- Minimal denitrogenation was obtained at the lowest severities practiced.
- The nickel molybdate catalyst provided higher levels of denitrogenation at equivalent desulfurization when compared to the cobalt molybdate catalyst.

## 2. M-SERIES STUDIES

### SUMMARY

Crude above-ground shale oil was processed for a nominal 100 hours at constant (target) operating conditions in order to evaluate initial catalyst stability, as well as to determine the length of time required to reach full catalyst equilibration. Studies were made over both cobalt molybdate and nickel molybdate hydrotreating catalysts. Both catalysts produced denitrogenation of about 10 percent and desulfurization of 60 to 70 percent, with the nickel molybdate catalyst showing slightly higher heteroatom removals at lower apparent hydrogen consumption. For both

catalysts, approximately 70 hours of operation were required for (apparent) equilibration of catalyst activity.

#### OBJECTIVES

Objectives for these runs were to: (1) examine initial catalyst stability parameters with respect to heteroatom removal, (2) determine the apparent time requirement for catalyst equilibration, (3) produce comparative data for cobalt molybdate and nickel molybdate catalysts and (4) produce adequate quantities of products for further processing and detailed evaluation.

#### UNIT DESCRIPTION

Nominal 1" I.D. trickle flow reactors, described in Subsection I, were used for the M-21 study (cobalt molybdate catalyst). No external guardbed was used; an internal tabular alumina preheat section was provided for this purpose.

The M-22 study (nickel molybdate catalyst) was also performed in nominal 1" hydrotreating systems, but with a slightly different configuration. These systems are described in detail in Section VI.

#### EXPERIMENTAL

Raw above-ground shale oil was hydrotreated at constant target conditions of 650°F, 2 LHSV, 3000 SCFB hydrogen circulation and 1000 psig total system pressure for both units. The charge was not filtered or pretreated in any way.



For run M-21 the reactor was packed with tabular alumina as postheat, and 150-ml of 1/8" Co/Mo catalyst void-filled with 150-ml of Ottawa sand were added. The remaining space in the reactor was filled with tabular alumina as preheat material.

Run M-22 was accomplished with a slightly smaller reactor charging 90-ml of nickel molybdate catalyst. Packing and void-filling procedures were followed in a manner analogous to that used for run M-21.

Pressure testing was accomplished to 1500 psig with nitrogen and hydrogen, after which the catalyst was sulfided to 700°F with H<sub>2</sub>S at bottle pressure for four hours. The unit was cooled with flowing hydrogen, hydrogen rate adjusted and the unit pressured to 1000 psig.

Samples of each material balance period were stabilized by heating under vacuum to 300°F for at least two hours. This method proved most effective at removing entrained water and dissolved H<sub>2</sub>S and NH<sub>3</sub> from the sample. Stabilized samples were submitted for total nitrogen and sulfur analysis. Material balances were performed every twelve hours early in each run and at 24 hour intervals thereafter.

Hydrotreated product from run M-21 was composited in bulk, mixed thoroughly and split into halves. Each half was fractionated on a batch still: one half to a 500°F nominal cut point and the other to a 600°F cut point.

Product from run M-22 was also composited and fractionated at 600°F atmospheric equivalent on the batch still to produce sample M-221.

#### FEEDSTOCK

Sufficient raw above-ground shale oil was mixed and withdrawn from drum #52-SH-06-01 and supplied to lab personnel as feed to hydrotreating runs M-21 and M-22. The raw oil was obtained from the original 14-drum Air Force shipment and its properties are shown in Table III-6.

#### RESULTS

Hydrotreating material balances for both runs are shown in Tables III-7 and III-8. Fractionation of the products and the detailed analysis of each is delineated in Tables III-9 through III-11. The reader should note that oxygen balances are calculated based on data obtained during Part 1 and Part 3 of this section and are not measured values.

Figure III-8 shows the sulfur and nitrogen removing activity of the cobalt molybdenum (M-21) catalyst. Figure III-9 shows similar data for the nickel molybdenum catalyst.

#### DISCUSSION

Both runs were reasonably stable through the approximately 100 hours of operation. Due to a slight operating difficulty during Run M-21, higher severities (+10°F and

TABLE III-6

M-21 AND M-22 HYDROTREATING  
SERIES FEED PROPERTIES OF  
CRUDE PARAHO SHALE OIL

GRAVITY, °API	21.1
SULFUR, WT. %	0.63
NITROGEN, WT. %	1.98
OXYGEN, WT. %	1.04

TABLE III-7  
CRUDE SHALE OIL HYDROTREATING  
SERIES M-21

Period	1	2	3	4	5	6
OPERATING CONDITIONS						
Temperature, °F	662	661	660	660	655	652
Pressure, PSIG	1005	1038	1029	1027	1018	1034
LHSV, Hr <sup>-1</sup>	1.70	1.75	1.76	1.88	1.85	1.74
H <sub>2</sub> Rate, SCFB	3570	3311	3440	3196	3260	3382
MATERIAL BALANCE						
	Weight Percent of Feed					
Feed	100	100	100	100	100	100
H <sub>2</sub> In	5.70	5.38	5.59	5.19	5.30	5.50
Subtotal In	105.70	105.38	105.59	105.19	105.30	105.50
H <sub>2</sub> O	(0.69)	(0.72)	(0.68)	(0.67)	(0.67)	(0.69)
NH <sub>3</sub>	(0.65)	(0.86)	(0.21)	(0.17)	(0.23)	(0.40)
H <sub>2</sub> S	(0.47)	(0.50)	(0.47)	(0.41)	(0.42)	(0.46)
H <sub>2</sub> Out	3.21	3.62	3.67	2.88	3.43	1.78
C <sub>1</sub>	0.09	-	-	0.03	0.01	-
C <sub>2</sub>	0.87	0.78	0.71	0.83	0.42	0.06
C <sub>3</sub>	1.13	0.50	1.04	0.69	0.24	0.04
C <sub>4</sub>	1.16	0.96	0.40	0.68	0.24	0.02
C <sub>5</sub>	1.07	0.18	0.54	0.43	0.04	-
Stabilized Liquid	93.35	88.62	96.61	99.50	98.35	93.43
Subtotal	103.10	97.18	104.73	106.67	104.44	96.83
Closure	97.5	92.2	99.2	101.4	99.2	91.8
Hydrogen Consumption, SCFB	1533	1085	1184	1425	1149	2288
PRODUCT PROPERTIES						
°API	25.4	25.1	24.7	25.1	24.3	24.5
Sulfur, Wt %	0.20	0.18	0.20	0.25	0.24	0.2
Nitrogen, Wt %	(1.533)	(1.423)	(1.861)	(1.836)	(1.809)	(1.7
Oxygen, Wt %	-	-	-	-	-	(0.4

( ) Calculated

TABLE III-8

# CRUDE SHALE OIL HYDROTREATING SERIES M-22

Period	1	2	3	4	5	6
OPERATING CONDITIONS						
Temperature, °F	650	650	650	650	650	650
Pressure, PSIG	1000	1000	1000	1000	1000	1000
LHSV, Hr <sup>-1</sup>	2	2	2	2	2	2
H <sub>2</sub> Rate, SCFB	3033	3062	3020	3024	3054	3038
MATERIAL BALANCE						
Weight Percent of Feed						
Feed	100	100	100	100	100	100
H <sub>2</sub> In	4.96	5.01	4.94	4.94	4.99	4.97
Subtotal In	104.96	105.01	104.94	104.94	104.99	104.97
H <sub>2</sub> O	(0.62)	(0.62)	(0.62)	(0.63)	(0.63)	(0.63)
NH <sub>3</sub>	(0.31)	(0.20)	(0.21)	(0.30)	(0.23)	(0.24)
H <sub>2</sub> S	(0.52)	(0.53)	(0.51)	(0.51)	(0.50)	(0.50)
H <sub>2</sub> Out	3.46	3.56	3.89	3.71	3.11	3.50
C <sub>1</sub>	-	-	-	-	-	-
C <sub>2</sub>	0.85	1.00	0.28	0.48	1.08	0.74
C <sub>3</sub>	0.74	0.74	0.20	0.44	1.00	0.66
C <sub>4</sub>	0.63	0.71	0.13	(0.53)	0.51	0.51
C <sub>5</sub>	0.89	0.49	0.39	0.57	1.69	0.90
Stabilized Liquid	99.00	100.19	98.90	97.91	98.11	98.63
Subtotal	107.02	108.04	105.13	105.05	106.71	106.31
Closure	102.0	102.9	100.2	100.1	101.6	101.3
Hydrogen Consumption, SCFB	912	880	641	755	1150	894
PRODUCT PROPERTIES						
°API	25.1	25.3	24.9	24.8	24.9	24.9
Sulfur, Wt %	0.14	0.13	0.15	0.15	0.16	0.16
Nitrogen, Wt %	(1.722)	(1.811)	(1.794)	(1.771)	(1.825)	(1.811)
Oxygen, Wt %	-	-	-	-	-	(0.49)

\* TOTAL

( ) CALCULATED

TABLE III-9

**CRUDE SHALE OIL HYDROTREATING**  
**SERIES M-21**  
**PRODUCT FRACTIONATION M-211**

<b>Fraction, °F</b>	<b>IBP- 500</b>	<b>500 +</b>
Yield, Wt % of Feed	14.8	80.9
Yield, LV % of Feed	16.6	91.2
°API	39.7	21.6
Carbon, Wt %	-	85.96
Hydrogen, Wt %	-	10.88
Nitrogen, Wt %	-	(2.05)
Basic Nitrogen, Wt %	-	1.266
Sulfur, Wt %	-	0.26
Oxygen, Wt %	-	-
Phenols, Wt %	-	-
Ramsbottom Carbon	-	1.18
Paraffins (P + N), LV %	-	-
Olefins, LV %	-	-
Naphthenes, LV %	-	-
Aromatics, LV %	-	-
Gross Heating Value, Btu/lb	-	-
	-	-

TABLE III-10

## CRUDE SHALE OIL HYDROTREATING

## SERIES M-21

## PRODUCT FRACTIONATION M-212

Fraction, °F	IBP-600	600 +
Yield, Wt % of Feed	29.5	66.2
Yield, LV % of Feed	32.3	65.6
°API	35.6	19.7
Carbon, Wt %	-	87.18
Hydrogen, Wt %	-	10.89
Nitrogen, Wt %	(1.27)	(2.10)
Basic Nitrogen, Wt %	1.14	1.338
Sulfur, Wt %	0.17	0.24
Oxygen, Wt %	-	-
Phenols, Wt %	-	-
Ramsbottom Carbon	-	1.42
Paraffins (P+N), LV %	-	-
Olefins, LV %	-	-
Naphthenes, LV %	-	-
Aromatics, LV %	-	-
Gross Heating Value, Btu/lb	-	-
Bromine Number	29	-

TABLE III-11

**CRUDE SHALE OIL HYDROTREATING**  
**SERIES M-22**  
**PRODUCT FRACTIONATION M-221**

Fraction, °F	IBP-600	600 +
Yield, Wt % of Feed	26.0	72.7
Yield, LV % of Feed	28.6	72.6
°API	36.6	20.9
Carbon, Wt %	-	87.5
Hydrogen, Wt %	-	10.1
Nitrogen, Wt %	(1.18)	(2.07)
Basic Nitrogen, Wt %	1.07	1.311
Sulfur, Wt %	0.15	0.15
Oxygen, Wt %	-	-
Phenols, Wt %	-	-
Ramsbottom Carbon	-	1.04
Paraffins (P + N), LV %	-	-
Olefins, LV %	-	-
Naphthenes, LV %	-	-
Aromatics, LV %	-	-
Gross Heating Value, Btu/lb	-	-
Bromine Number	27	-



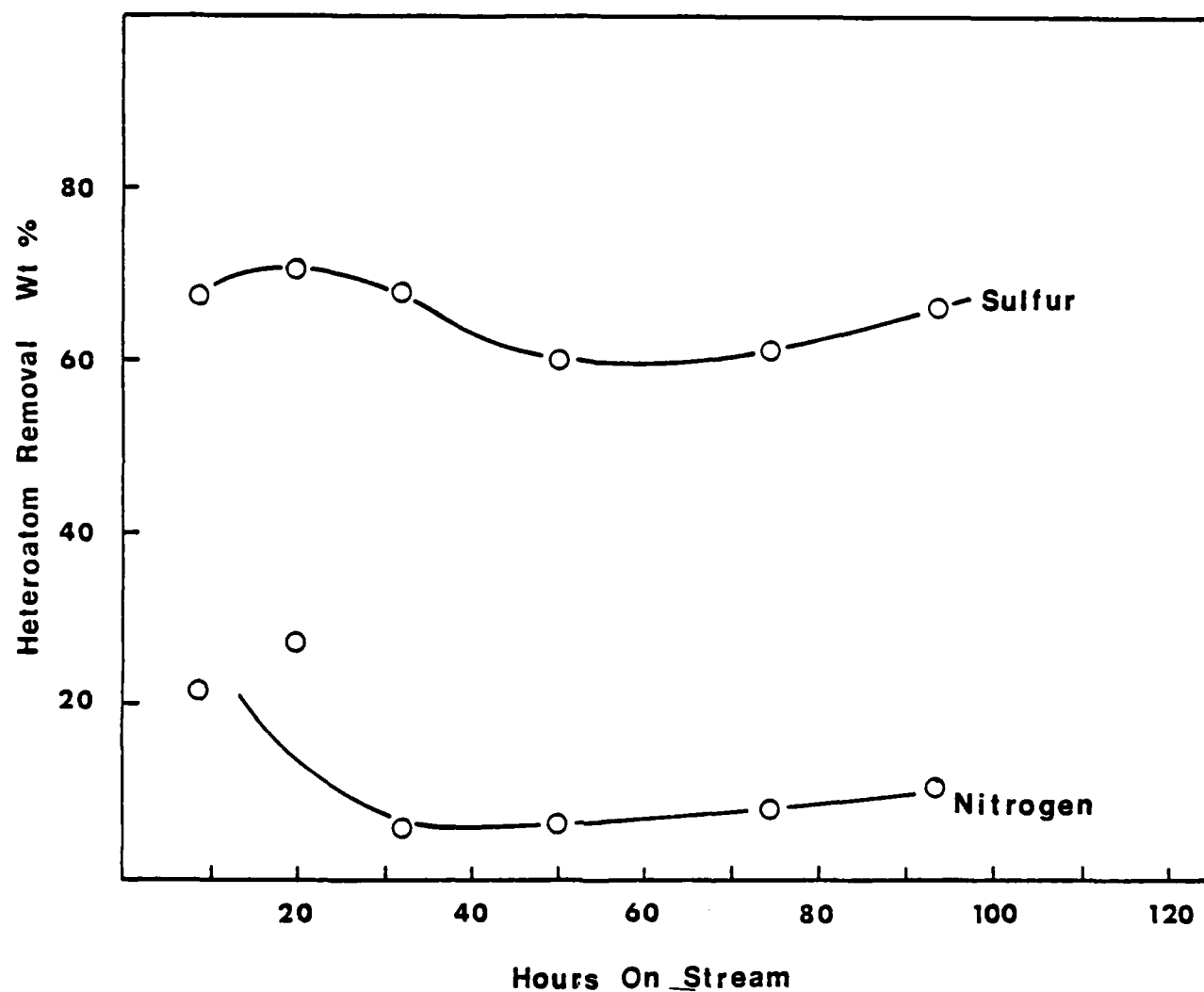
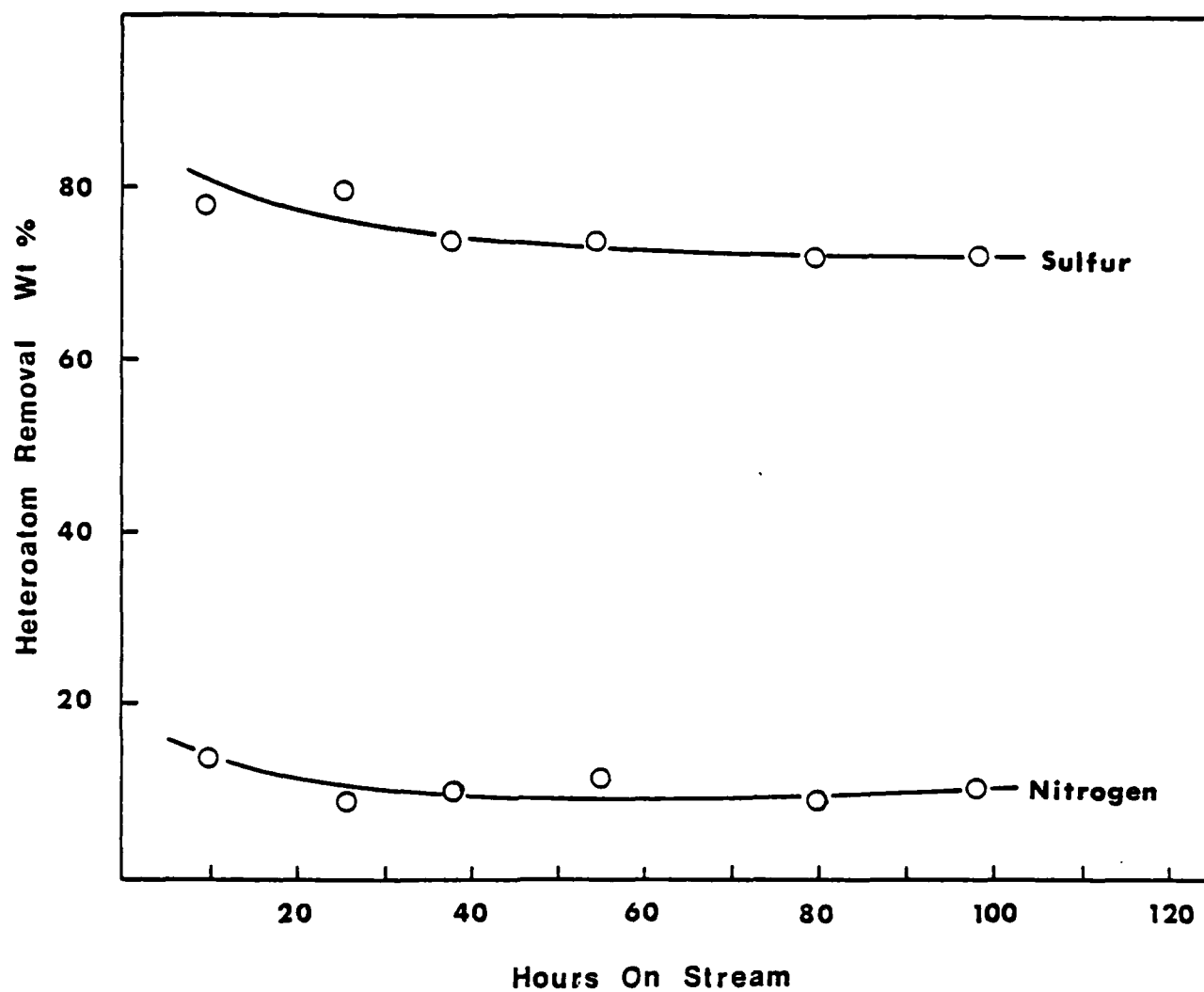


Figure III-8. Heteroatom Removal Stability:  
Crude Shale Oil Hydrotreating - Series M-21



**Figure III-9. Heteroatom Removal Stability:  
Crude Shale Oil Hydrotreating - Series M-22**

-0.25 LHSV) were used than in Run M-22. As a result, higher nitrogen removal and hydrogen consumption was encountered in Run M-21. There also appeared to be a gain in catalyst activity later in the M-21 study, indicating that other experimental problems may have existed than the operator noticed. The high sulfur results in Series M-21 are thought to be due to incomplete stripping of water and  $H_2S$  from the products.

Results from these studies indicate that the parameter variation data will most probably overstate denitrogenation capabilities of a lined-out catalyst system.

### 3. CRUDE SHALE OIL HYDROTREATING - 30-DAY AGING STUDY

#### SUMMARY

During the month of October 1979, the Synthetic Oils Research Group successfully maintained continuous operation of a 1" Universal reactor in order to examine the rate of activity decay of a commercial hydrotreating catalyst (Co/Mo) while refining crude Paraho Shale Oil. The achievement provided data necessary to determine the life expectancy of the catalyst under one set of operating conditions.

The shale oil feed was an above-ground retorted oil supplied by the government and was produced at the Paraho retort, Anvil Points facility. One full drum of Paraho oil, assigned Synthetic Oils #52-SH-07-01, was used exclusively over the course of the run.

Product samples were analyzed daily for sulfur and nitrogen content in order to determine  $H_2S$  and  $NH_3$  production during the run and in essence the effectiveness of the hydrotreatment under the existing conditions. The bulk of the product was composited in five gallon cans and retained. Selected composites were delivered to the Ashland Oil Research Pilot Plant and treated on their catalytic cracking unit.

#### OBJECTIVES

Crude Paraho shale oil was hydrotreated at constant conditions for an extended period in order better to define operating parameters for the crude shale hydrotreater module. Specific objectives were to demonstrate the hydrotreating stability of Co/Mo catalyst as gauged by heteroatom and arsenic removal while producing sufficient quantities of product for further processing.

#### MECHANICAL DESCRIPTION

The arrangement of hydrotreater unit components is identical to that used in Volume II, Section III, Part 3.

Two parallel guardbeds were installed in the system such that the hydrogen/oil mixture passed upflow through one guardbed, then directly downflow through the reactor. The parallel arrangement provided the convenience of performing guardbed maintenance without interrupting unit operation. Each guardbed was comprised of a four foot length of 3/4" O.D. 316 stainless steel tubing packed with 170-180

ml of 1/8" activated alumina extrudate supported at top and bottom by plugs of stainless steel wool. The active guardbed was maintained at 500°F. The beds were intended to remove some arsenic, iron and other metals from the shale oil feed before entering the Universal reactor pre-heat zone.

The 1" Universal reactor was packed first with inert tabular alumina. Onto this layer was added 100-ml of 1/16" cobalt molybdate catalyst and 100-ml of Ottawa sand void filler in alternating 10-ml increments. Finally, tabular alumina was used to fill the remaining space in the reactor.

#### CHEMICAL/CATALYST DESCRIPTION

Hydrogen and the crude Paraho oil (without any prior purification) were passed through a guardbed and into a 1" Universal reactor. Each guardbed was packed in a random fashion with 170-180-ml of 1/8" commercially available activated alumina extrudate.

The Universal reactor was packed such that the cobalt molybdate catalyst bed was centered in the reactor body. The catalyst bed was void-filled with commercially available Ottawa sand and the mixture was positioned between columns of inert tabular alumina catalyst support.

Properties of the feed oil are shown in Table III-12.

**TABLE III-12**

**RAW CRUDE PARAHO SHALE OIL  
(#52-SH-07-01) PROPERTY ANALYSIS**

GRAVITY, °API	20.3
ELEMENTAL, WT. %:	
NITROGEN	1.91
SULFUR	0.62
OXYGEN	1.04
RAMSBOTTOM CARBON, WT. %	1.98
ARSENIC, PPM	17
BASIC NITROGEN, WT. %	1.25
AROMATICS, VOL. %	58.9

## EXPERIMENTAL

The Universal reactor was operated for 27 consecutive days (October 5 - November 1, 1979) at constant target conditions of 675°F, 1000 psig pressure, 2 LHSV and 3000 SCFB hydrogen rate.

After pressure testing the system, first with nitrogen then hydrogen to 1500 psig, the catalyst was presulfided with H<sub>2</sub>S at bottle pressure and increasing temperatures up to 725°F for three hours. The reactor was allowed to cool nearly to room temperature, guardbeds were pressure checked independently and connected to the reactor, and the whole system was slowly brought up to the desired conditions. A five hour lineout allowance was given before the start of the first material balance period.

Samples of the liquid product (~100 ml) were stripped by heating at 300-350°F for at least two hours at total reflux. Stable product from each 24 hour material balance period was then analyzed for sulfur and nitrogen content. These properties, along with API gravity, were charted during the run. Samples of the reactor off-gas for each balance period were subjected to complete GC gas analysis.

A descriptive account of day-by-day activities affecting the experiment divulges some of the details of the run sequence and the complications encountered.

Packing of the reactor, pressure testing and sulfiding operations described previously were completed in time to begin oil flow to the unit on October 2. Pumping problems were encountered immediately due to feed viscosity; pre-heating the feed with a heat lamp rectified the situation. Within four hours of start-up a plug developed in the active guardbed (as evidenced by an 800 psig pressure drop across the reactor) requiring a switch to the alternate bed while the plugged bed was repacked. Within the next 32 hours the same event occurred twice, finally resulting in reactor shutdown on October 3.

After cooling, the main reactor was dumped, cleaned and repacked, then was pressure tested, presulfided, and readied for use by October 5. During this down time the guardbeds were repacked in a looser manner to alleviate prior plugging problems. The run was restarted on October 5 at 2155 hours and continued uninterrupted through November 1. All material balance data presented are based on this (October 5) start-up date.

Other minor problems occurred with regularity. For example:

- Wet test meters used for quantifying off-gas rates were replaced as indicated below. Each meter change resulted in a small but finite loss of gases. Low water levels also resulted in generally low readings.



October 6 at 1100 hrs. - internal pressure build-up

October 16 at 1520 hrs. - needle malfunction

October 20 at 1030 hrs. - low water level

October 24 at 2105 hrs. - low water level

October 29 at 0850 hrs. - low water level

- Feed pump problems resulted in oil flow stoppage at the following periods:

October 1 at 0155 hrs. - pump rebuilt

October 9 at 0355 hrs. - lost prime

October 10 at 1355 hrs. - lost prime

October 12 at 0155 hrs. - lost prime

November 1 at 0355 hrs. - lost prime

- Numerous instances of Grove back-pressure regulator problems were encountered:

October 6 at 1655 hrs. - low dome pressure

October 7 at 1055 hrs. - low dome pressure

October 9 at 1355 hrs. - low dome pressure

October 10 at 1130 hrs. - low dome pressure

October 24 at 1730 hrs. - malfunction,  
replaced

October 28 at 0005 hrs. - low dome pressure

- High water content in the feed drum presented some difficulty as noted in two instances in the log (October 11, 13).
- Guardbed temperature control by sensing the bed skin temperature proved a difficult endeavor. On two occasions, guardbed problems resulted in some reactor down time. Beds were changed:

October 24 at 0355 hrs. - severe bed plug

October 26 at 0955 hrs. - outlet valve  
malfunction

## RESULTS

The process and analytical data are shown in Tables III-13 through III-21 and Figures III-10 and III-11.

Analytical data reported in Table III-18 refer to alumina from the guardbed in service when the run was completed. The bed was emptied in segments (top, middle, bottom) and each was analyzed separately. The same dumping procedure was followed in the cases of reactor preheat zone (Table III-19) and catalyst zone (Table III-20).

It should be noted from Figure III-10 that "Reactor Temperature" is a time-weighted average of the temperatures of the upper and lower portions of the catalyst bed. In that same figure, "Reactor Pressure" is again a time-weighted average of reactor inlet and outlet pressures.

**TABLE III-13**  
**30-DAY RUN MATERIAL BALANCES**

Period	1	2	3	4	5	6	7	8	9	10	11	12
<b>OPERATING CONDITIONS</b>												
Temperature, °F	678	678	679	677	676	676	676	676	675	675	676	676
Pressure, PSIG	994	1004	1012	1014	1009	1036	1026	1026	1041	1037	1025	1049
LHSV, Hr <sup>-1</sup>	2.00	1.96	2.04	2.19	1.80	1.74	1.72	2.02	1.93	1.77	1.93	1.95
Hydrogen Rate, SCFB	3018	3051	2941	2724	3306	3380	3551	2965	3136	3427	3166	3140
<b>MATERIAL BALANCE</b>												
<b>Weight Percent of Feed</b>												
Feed	100	100	100	100	100	100	100	100	100	100	100	100
Hydrogen In	4.88	4.93	4.76	4.40	5.35	5.47	5.74	4.79	5.07	5.54	5.12	5.08
Subtotal In	104.88	104.93	104.76	104.40	105.35	105.47	105.74	104.79	105.07	105.54	105.12	105.08
H <sub>2</sub> O	(0.73)	(0.78)	(0.74)	(0.72)	(0.72)	(0.72)	(0.73)	(0.72)	(0.72)	(0.72)	(0.73)	(0.72)
H <sub>2</sub> S	(0.45)	(0.48)	(0.48)	(0.47)	(0.24)	(0.44)	(0.47)	(0.43)	(0.45)	(0.42)	(0.43)	(0.40)
NH <sub>3</sub>	(0.29)	(0.34)	(0.35)	(0.22)	(0.18)	(0.18)	(0.30)	(0.22)	(0.17)	(0.22)	(0.27)	(0.18)
Hydrogen Out	3.21	2.86	2.91	2.57	3.36	3.17	3.90	2.91	2.94	2.71	2.43	3.55
C <sub>1</sub>	0.25	-	-	0.05	-	0.23	-	-	0.92	0.26	-	-
C <sub>2</sub>	0.10	0.75	0.20	0.07	0.09	0.25	0.27	0.32	0.06	0.08	0.33	0.40
C <sub>3</sub>	0.06	0.68	0.16	0.05	0.11	0.22	0.18	0.22	0.05	0.06	0.17	0.34
C <sub>4</sub>	0.02	0.62	0.05	0.23	0.08	0.24	0.10	0.19	-	0.02	0.12	0.24
C <sub>5</sub>	-	-	0.09	-	-	0.10	0.52	0.13	-	-	0.29	-
Stabilized Liquid	96.74	85.70	94.36	98.90	99.30	99.51	96.89	98.91	100.13	99.16	97.50	99.17
Subtotal Out, %w	101.85	92.41	99.34	103.28	104.08	105.06	103.36	104.05	105.44	103.65	102.27	105.00
Closure, %w	97.1	88.1	94.8	98.9	98.8	99.6	97.7	99.3	100.4	98.2	97.3	99.9
OAPI	25.0	25.0	25.0	25.0	24.3	24.4	24.6	24.5	24.8	24.5	24.7	24.5
Sulfur, %w	(0.2)	(0.2)	0.18	0.18	0.40	0.21	0.18	0.22	0.20	0.23	0.22	0.24
Nitrogen, %w	(1.8)	(1.8)	(1.80)	(1.82)	(1.85)	(1.84)	(1.79)	(1.82)	(1.84)	(1.82)	(1.81)	(1.85)
Basic Nitrogen, %w	-	-	1.32	-	-	-	-	-	1.29	-	-	-
Hydrogen Consumption, SCFB	1031	1282	1144	1137	1229	1422	1140	1163	1318	1750	1662	943

( ) ESTIMATED OR CALCULATED DATA

**TABLE III-13 (cont'd)**  
**30-DAY RUN MATERIAL BALANCES**

Period	13	14	15	16	17	18	19	20	21	22	23	24
<b>OPERATING CONDITIONS</b>												
Temperature, °F	676	675	675	675	675	675	675	676	677	676	676	675
Pressure, PSIG	1047	1048	1044	1038	1044	1080	1073	1040	1034	1054	1020	1045
LHSV, Hr <sup>-1</sup>	1.89	1.99	1.91	1.83	1.93	1.70	2.18	1.87	1.89	1.87	1.86	1.93
Hydrogen Rate, SCFB	3.80	3087	3175	3320	3152	3442	2684	3217	3150	3231	3287	3151
<b>MATERIAL BALANCE</b>												
<b>Weight Percent of Feed</b>												
Feed	100	100	100	100	100	100	100	100	100	100	100	100
Hydrogen In	5.14	4.99	5.13	5.37	5.10	5.57	4.34	5.20	5.09	5.22	5.32	5.09
Subtotal In	105.14	104.99	105.13	105.37	105.10	105.57	104.34	105.20	105.09	105.22	105.32	105.09
H <sub>2</sub> O	(0.72)	(0.71)	(0.73)	(0.72)	(0.74)	(0.69)	(0.73)	(0.73)	(0.73)	(0.72)	(0.73)	(0.73)
H <sub>2</sub> S	(0.39)	(0.49)	(0.39)	(0.43)	(0.37)	(0.41)	(0.34)	(0.38)	(0.53)	(0.43)	(0.53)	(0.40)
NH <sub>3</sub>	(0.18)	(0.16)	(0.23)	(0.15)	(0.24)	(0.02)	(0.27)	(0.17)	(0.17)	(0.37)	(0.08)	(0.22)
Hydrogen Out	3.57	3.39	3.38	3.78	3.52	3.80	3.03	3.59	3.26	3.69	3.74	3.67
C1	0.09	-	-	0.11	0.08	0.09	0.07	0.11	0.10	-	0.34	0.18
C2	0.15	0.09	0.05	0.08	0.07	0.07	0.07	0.09	0.04	0.12	0.13	0.01
C3	-	0.09	0.04	0.06	0.05	0.06	0.04	0.07	0.01	0.10	0.08	0.20
C4	0.82	0.08	-	0.15	0.04	0.02	0.15	0.04	0.01	0.04	0.17	0.05
C5	-	0.09	-	-	-	-	-	-	0.01	0.23	0.01	-
Stabilized Liquid	100.18	101.11	98.49	100.36	95.42	105.71	96.95	98.49	97.08	98.96	98.18	98.49
Subtotal Out, %w	106.10	106.21	103.31	105.84	100.53	110.87	101.65	103.67	102.04	104.66	103.99	103.95
Closure, %w	100.9	101.2	98.3	100.4	95.7	105.0	97.4	98.5	97.1	99.5	98.7	98.9
OAPI	24.5	24.4	24.6	24.5	24.5	24.4	24.2	24.2	24.3	24.9	24.0	24.2
Sulfur, %w	0.25	0.16	0.26	0.21	0.28	0.22	0.31	0.27	0.12	0.22	0.12	0.25
Nitrogen, %w	(1.83)	(1.83)	(1.82)	(1.85)	(1.87)	(1.86)	(1.82)	(1.87)	(1.90)	(1.70)	(1.95)	(1.83)
Basic Nitrogen, %w	-	1.32	-	-	-	1.35	-	-	-	-	1.34	-
Hydrogen Consumption, SCFB	972	988	1082	982	976	1093	807	994	1131	947	972	879

TABLE III-13 (cont'd)

## 30-DAY RUN MATERIAL BALANCES

Period	25	26	27	28	29	30
OPERATING CONDITIONS						
Temperature, °F	675	675	675			
Pressure, PSIG	1031	1031	1039			
LHSV, Hr <sup>-1</sup>	2.03	2.20	2.13			
Hydrogen Rate, SCFB	2942	2793	2864			
MATERIAL BALANCE						
Weight Percent of Feed						
Feed	100	100	100			
Hydrogen In	4.76	4.52	4.63			
Subtotal In	104.76	104.52	104.63			
H <sub>2</sub> O	(0.73)	(0.73)	(0.72)			
H <sub>2</sub> S	(0.40)	(0.36)	(0.35)			
NH <sub>3</sub>	(0.18)	(0.14)	(0.12)			
Hydrogen Out	3.34	3.21	3.25			
C1	0.28	-	0.12			
C2	0.04	0.28	0.18			
C3	0.10	0.21	0.13			
C4	0.03	0.10	0.09			
C5	0.02	-	-			
Stabilized Liquid	97.67	98.40	98.65			
Subtotal Out, %w	102.79	103.43	103.61			
Closure, %w	98.1	99.0	99.0			
OAPI	24.0	23.9	24.1			
Sulfur, %w	0.25	0.28	0.29			
Nitrogen, %w	(1.88)	(1.90)	(1.91)			
Basic Nitrogen, %w	-	-	1.34			
Hydrogen Consumption, SCFB	879	807	854			

TABLE III-14

**COMPOSITE PRODUCT INSPECTION**  
**COMPOSITE 1**  
**PERIODS 1-4**

Fraction, °F	-600	+ 600
Yield, Wt % of Feed	23.8	70.1
Yield, LV % of Feed	26.4	70.3
°API	37.0	20.7
Carbon, Wt %	-	-
Hydrogen, Wt %	13.1	-
Nitrogen, Wt %	(1.65)	(2.13)
Basic Nitrogen, Wt %	1.12	1.33
Sulfur, Wt %	0.14	0.21
Oxygen, Wt %	-	-
Phenols, Wt %	-	-
Ramsbottom Carbon	-	1.50
Paraffins (P+N), LV %	-	-
Olefins, LV %	-	-
Naphthenes, LV %	-	-
Aromatics, LV %	-	84.5
Gross Heating Value, Btu/lb	-	-
Arsenic, ppm	115 <sup>1.</sup>	34 <sup>1.</sup>

1. Values are suspected in error.

TABLE III-15

**COMPOSITE PRODUCT INSPECTION**  
**COMPOSITE 3**  
**PERIODS** 10-12

Fraction, °F	-600	+ 600
Yield, Wt % of Feed	26.7	71.8
Yield, LV % of Feed	29.7	71.9
°API	37.3	20.5
Carbon, Wt %	-	-
Hydrogen, Wt %	13.1	-
Nitrogen, Wt %	(1.69)	(2.20)
Basic Nitrogen, Wt %	1.20	1.33
Sulfur, Wt %	0.13	0.23
Oxygen, Wt %	-	-
Phenols, Wt %	-	-
Ramsbottom Carbon	-	1.61
Paraffins (P+N), LV %	-	-
Olefins, LV %	--	-
Naphthenes, LV %	-	-
Aromatics, LV %	-	65.5
Gross Heating Value, Btu/lb	-	-
Arsenic, ppb	10	400

TABLE III-16

**COMPOSITE PRODUCT INSPECTION**  
**COMPOSITE 7**  
**PERIODS** 26-27

Fraction, °F	-600	+ 600
Yield, Wt % of Feed	21.7	76.8
Yield, LV % of Feed	24.1	76.7
°API	37.6	20.1
Carbon, Wt %	-	-
Hydrogen, Wt %	13.0	-
Nitrogen, Wt %	(1.75)	(2.24)
Basic Nitrogen, Wt %	1.21	1.34
Sulfur, Wt %	0.17	0.26
Oxygen, Wt %	-	-
Phenols, Wt %	-	-
Ramsbottom Carbon	-	1.70
Paraffins (P + N), LV %	-	-
Olefins, LV %	-	-
Naphthenes, LV %	-	-
Aromatics, LV %	-	68.2
Gross Heating Value, Btu/lb	-	-
Arsenic, ppb	11	3000



TABLE III-17

COBALT MOLYBDATE  
HYDROTREATING CATALYST

FRESH CATALYST COMPOSITION

MoO <sub>3</sub>	12.5% WT
CoO	3.5% WT
Na <sub>2</sub> O	0.08% WT
Fe	0.03% WT
SiO <sub>2</sub>	1.5% WT
Al <sub>2</sub> O <sub>3</sub>	Balance

TABLE III-18

GUARDBED ALUMINA (ACTIVATED)

CHEMICAL ANALYSIS

	TOP 1/3 OF <u>GUARDBED</u>	MIDDLE 1/3 OF <u>GUARDBED</u>	BOTTOM 1/3 OF <u>GUARDBED</u>
PERIOD IN SERVICE	10/23-11/1	10/23-11/1	10/23-11/1
ARSENIC, WT. %	0.10	0.02	0.08
CARBON, WT. %	31.36	22.44	30.44
IRON, WT. %	0.89	0.23	0.27

# TABLE III-19

## PREHEAT ALUMINA (TABULAR)

### CHEMICAL ANALYSIS

	TOP 1/3 OF <u>PREHEAT</u>	MIDDLE 1/3 OF <u>PREHEAT</u>	BOTTOM 1/3 OF <u>PREHEAT</u>
PERIOD IN SERVICE	10/5-11/1	10/5-11/1	10/5-11/1
ARSENIC, WT. %	<0.01	<0.01	<0.01
CARBON, WT. %	0.78	0.56	0.50
IRON, WT. %	0.01	0.01	0.02

**TABLE III-20**  
**COBALT MOLYBDATE CATALYST**  
**CHEMICAL ANALYSIS**

	UPPER 1/3 OF CATALYST BED	MIDDLE 1/3 OF CATALYST BED	BOTTOM 1/3 OF CATALYST BED
ARSENIC, WT. %	0.34	0.12	0.09
CARBON, WT. %	16.5	15.5	19.2
IRON, WT. %	1.03	0.80	0.71

TABLE III-21

## CATALYST PHYSICAL PROPERTY ANALYSIS

	<u>FRESH</u>		<u>REGENERATED</u>		<u>SPENT</u>	
SURFACE AREA, M <sup>2</sup> /gm	270		201		18	
PORE VOLUME, cc/gm	0.65		0.49		0.06	
PORE DIAM $\overset{\circ}{\text{A}}$	<u>% DIST</u>	<u>PV, CC/GM</u>	<u>% DIST</u>	<u>PV, CC/GM</u>	<u>% DIST</u>	<u>PV, CC/GM</u>
>6000	DATA NOT AVAILABLE		0	0	0	0
6000-1000			1.487	0.007	1.852	0.001
1000-400			2.230	0.011	11.111	0.006
400-200			3.717	0.018	9.259	0.005
200-100			8.922	0.044	5.557	0.003
100-80			48.699	0.238	11.111	0.006
80-60			30.855	0.151	24.074	0.014
60-40			4.089	0.020	25.926	0.015
40-35			0	0	5.556	0.003
35-30			0	0	5.556	0.003

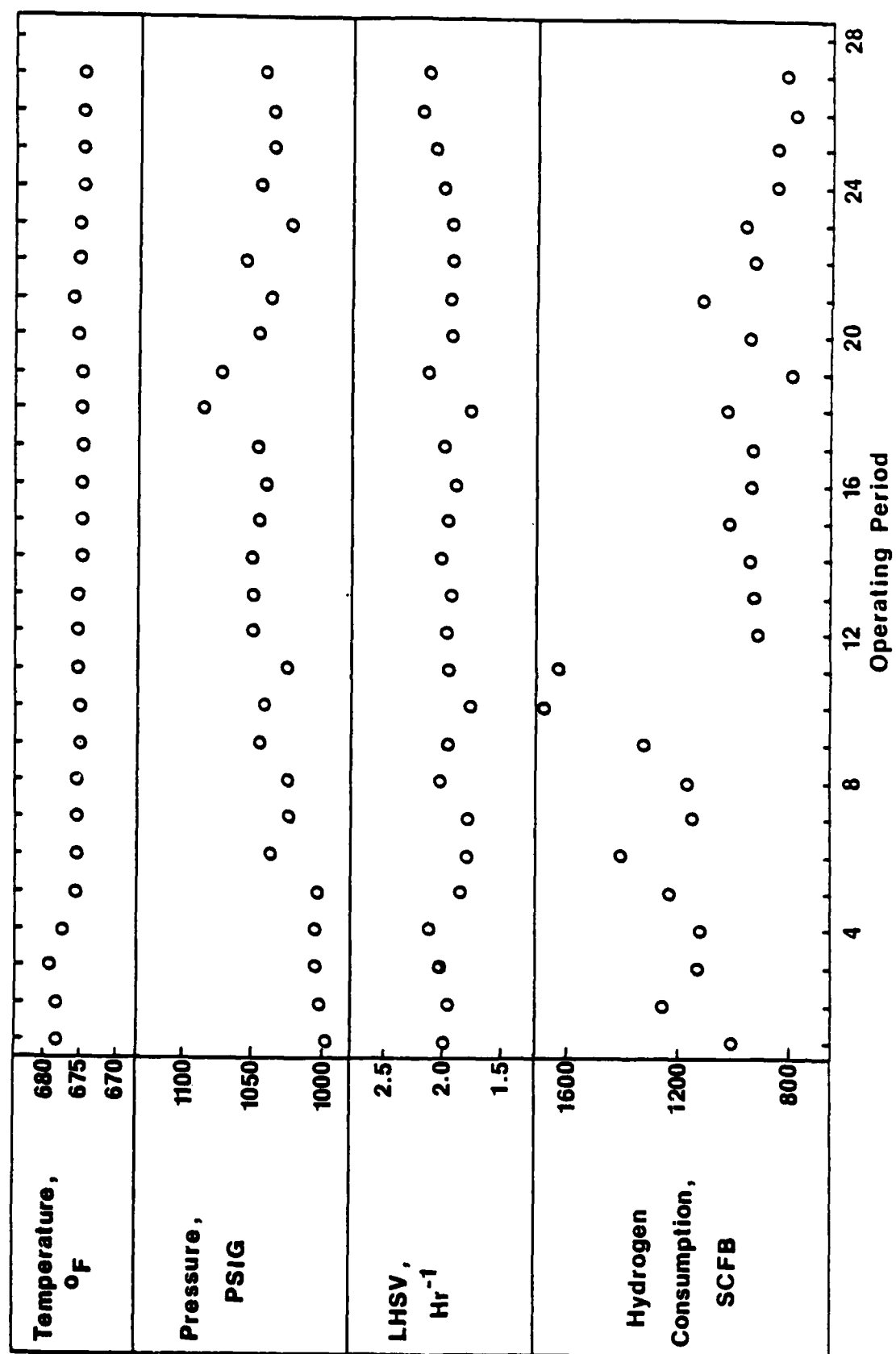


Figure III-10. CSHT Aging Results For Above-ground Shale Oil

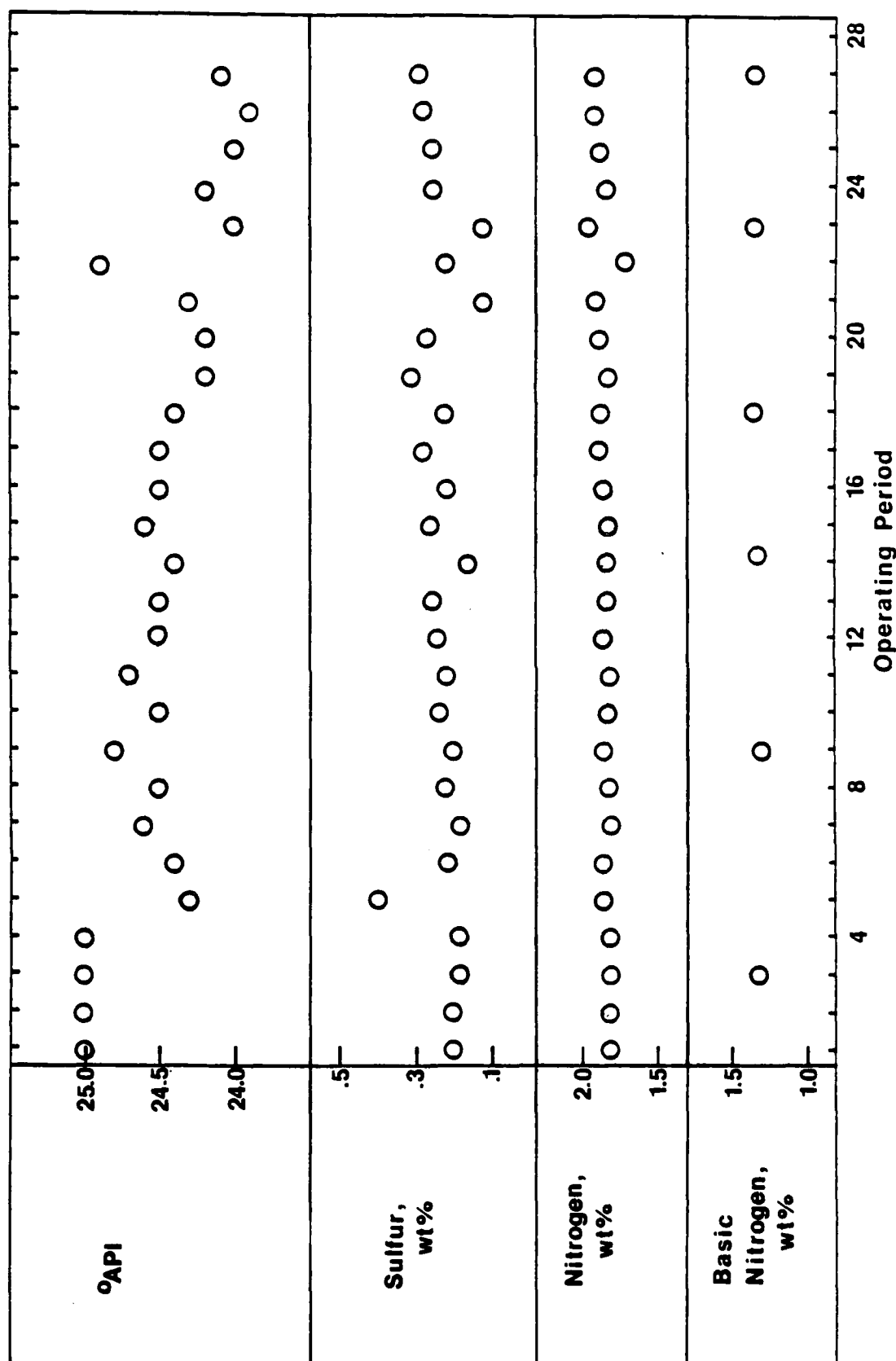


Figure III-11. CSHT Aging Results For Above-ground Shale Oil

## DISCUSSION

Activity decay of the cobalt molybdate catalyst occurred gradually over the course of the 27-day experiment. Evidence of gradual decay can be seen in the graphs of product gravity, sulfur and nitrogen content found in Figure III-11. Basic nitrogen values obtained on samples from selected periods in the run followed near to the same deactivation slope.

One of the most favorable aspects of the EXTRACTA-CRACKING process is its minimal hydrogen consumption, owing in part to the mild conditions encountered in the crude shale hydrotreater module. This aging run simulates the conditions anticipated for the crude hydrotreater and demonstrates that chemically bound nitrogen components can be altered to an entity easily removed by acid extraction.

The guardbed installation proved beneficial in that some arsenic and iron were prevented from entering the reactor proper. As seen in Tables III-18 through III-20, arsenic and iron were deposited heavily in guardbed and reactor catalyst zones while very little was detected in the preheat zone where coking problems are often encountered with the equipment in use.

Hydrogen consumption values varied from 807 to 1750 SCFB with an average consumption of 1096 SCFB. The results (Figure III-10) are consistent except for the periods 10 and 11 when some hydrogen flow control problems occurred.



#### CONCLUSIONS/RECOMMENDATIONS

- Catalyst deactivation occurred gradually over the 27 days of continuous operation.
- Analytical comparison reveals that a larger percentage of total nitrogens are basic in the product than in the feed.
- The activated alumina guardbed succeeds in removing substantial amounts of arsenic and metals.
- Calculated hydrogen consumption is consistent and compares with other published data.
- Material balance closures are favorably consistent.

## SECTION IV

### FLUID CATALYTIC CRACKING OF ABOVE-GROUND SHALE OIL

A major key of the EXTRACTACRACKING process is fluid catalytic cracking (FCC) of high-nitrogen feedstocks. Objectives for this module are to convert an economic maximum of gas oil and heavier material into jet fuel and gasoline boiling range products. Secondary objectives for the FCC module are reduction of heteroatoms (sulfur, nitrogen, oxygen) without hydrotreating, and selectively redistributing the available hydrogen already in the heavy shale fractions so that the distillate product exhibits a hydrogen content greater than the FCC feed, again without external addition of hydrogen.

Due to the short experimental time available, which required a priori definition of experimental conditions with little opportunity for feedback from other process modules, a wide range of conditions and experimentation was provided. Fluid catalytic cracking studies were provided in the following manner:

1. Microactivity tests - provide yield-response curves as a function of feedstock, hydrotreater severity and FCC severity.
2. FCC M-series tests - provide single condition source specific data, including detailed product properties and material for further processing, as a function of hydrotreater catalyst and fractionator endpoint.

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REFINING OF MILITARY JET FUELS FROM SHALE OIL PART II

2/3

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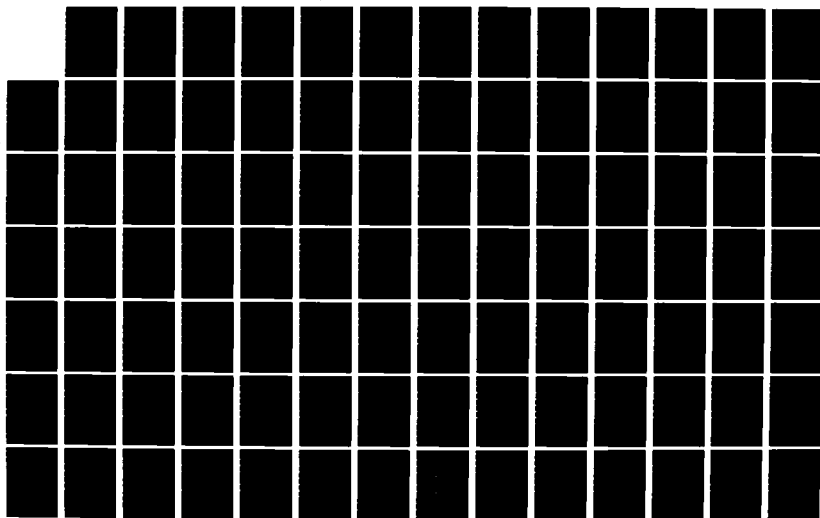
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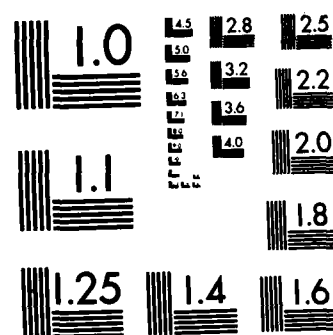
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3. FCR PHO tests - provide single condition source specific data, including detailed product properties and material for further processing as a function of hydrotreater catalyst age. Charging the unfractionated crude shale hydrotreater product to the FCC unit was evaluated.
4. MAT recycle tests - provide yield response data for selected recycle streams.

Test sets 1-3 are fresh-feed basis tests, while test set 4 evaluates options available on an independent recycle basis. Test sets 2 and 3 provide independent comparison of continuous versus MAT (batch) data, and allows some normalization and/or confirmation of the smaller scale data.

#### 1. MAT TESTS - FRESH FEED

##### SUMMARY

A total of 29 catalytic cracking data points have been developed for 600°F+ hydrotreated above-ground shale oil. Operating severities were varied, producing conversions ranging from 32 to 86 weight percent based on 600°F+ feedstock. Complete yield structures were developed for each run in order to develop relative yield and selectivity curves for each feedstock.

##### OBJECTIVES

Target objectives for these studies were to develop, in a rapid manner, FCC yield response parameters for crude

shale hydrotreater products as a function of hydrotreater severity, boiling fraction, nitrogen content and FCC unit severity.

#### MECHANICAL DESCRIPTION

The MAT small-scale screening runs were carried out in the 15 mm I.D., 38 cm length quartz reactor of a Micro Activity Test (MAT) Unit of the type used for some years by oil industry and catalyst manufacturer research laboratories. This "MAT" is not universally standardized, but one version has been recommended for acceptance as a standard by the ASTM D-32 committee on catalysts. The reactor is positioned vertically. A 2-to-8 gram charge of molecular-sieve-containing (and/or amorphous) fluidized bed type cracking catalyst is held stationary in a constant temperature zone of an electrically heated furnace. Feedstock in the amount of 0.5 to 4 grams is delivered at constant rate downflow from a syringe. The feed oil should be vaporized before contact with the catalyst. Vaporization is accomplished by low-voltage resistance heating of the 18 gauge stainless steel tubing of a deadman-preheater insert above the catalyst bed within the quartz reactor. Product synthetic crude liquid is condensed and where necessary weathered at the end of the on-stream period. Gas produced is collected and measured above brine solution in a calibrated Pyrex vessel.

## EXPERIMENTAL

For each sample submitted to MAT analysis, a range of conditions comprising varying temperature, catalyst-to-oil ratio and/or WHSV was selected based on a priori estimation of conditions required to obtain 30 to 90 percent conversion. Each data point was evaluated and repeated if necessary. Additional runs were performed as needed to define the "knee" or maximum distillate liquid yield region.

For each run, the standard catalyst (an equilibrium commercial FCC sample) was regenerated in a muffle furnace for 2 hours at 1100°F. The catalyst charge was placed in the MAT unit, pressure tested and purged with nitrogen. After equilibration at temperature, feed was injected and the unit nitrogen-purged to four times the total system volume.

Product liquids were collected in tared liquid traps, and analyzed by a gravimeter and simulated distillation (ASTM D-2887). Product gas was collected via calibrated brine displacement and gas chromatography. Coke yield was measured by carbon content of the recovered catalyst.

Yield calculations and data reported were based on the specified feed cut point. The material lighter than the specified cut point is assumed to be unreactive.

### FEEDSTOCK

Three feedstocks were used for these tests. The evaluation sequence was designed to evaluate options available in the crude shale hydrotreater, in particular severity and catalyst.

As shown in Table IV-1, three fresh-feed chargestocks were evaluated. The M-212 sample was prepared over cobalt molybdate catalyst during the M-Series hydrotreating runs, and is analogous to the sample used for later FCR processing. The M-221 sample was prepared over nickel molybdate catalyst also during the M-Series hydrotreating runs, and also analogous to the FCR sample processed under that number. Finally, sample 2135 was prepared during the parameter variation hydrotreating studies over cobalt molybdate catalyst at very high severity to allow comparison of the effect of hydrotreater severity. All samples were fractionated to a nominal 600°F cut point, with the 600°F+ fraction used for these tests.

### RESULTS

Detailed results and graphical presentations of these data are shown in Tables IV-2, IV-3 and IV-4 and Figures IV-1 through IV-6.

### DISCUSSION

Results from these tests show no unexpected trends. For the range of conversions obtained, smooth curves were derived for all data. The materials produced during higher



**TABLE IV-1****MICROACTIVITY TESTS  
FRESH FEEDSTOCK**

<b>Sample</b>	<b>M- 212</b>	<b>2135</b>	<b>M-221</b>
<b>°API</b>	19.7	28.8	20.9
<b>Carbon</b>	87.2		87.5
<b>Hydrogen</b>	10.9		10.1
<b>Nitrogen</b>	(2.10)	.80	(2.065)
<b>Basic Nitrogen</b>	1.338	.40	1.311
<b>Sulfur</b>	0.24	.0098	0.15
<b>Simulated Distillation, °F</b>			
<b>IBP</b>	569	390	594
<b>10</b>	666	582	640
<b>50</b>	829	735	804
<b>90</b>	985	917	958
<b>EP</b>	>1020	998	1013

**All units are weight percent unless specified**

**TABLE IV-2**  
**PHASE II MAT SUMMARY - M212**

RUN NO.	109	110	111	112	113	114	115	116	131	132
<u>CATALYST/FEEDSTOCK</u> <u>CONDITIONS</u>										
TEMP., °F	950	950	1000	1000	950	950	100	1000	1050	1050
CAT./OIL	3.0	3.0	3.0	3.0	5.4	5.3	5.3	5.5	6.0	5.6
WHSV	15.8	15.4	15.7	15.8	8.9	9.1	9.1	8.7	8.1	8.5
<u>TEST RESULTS</u>										
RECOVERY, WT%	96.3	96.8	96.2	100.1	94.1	99.4	90.0	95.5	89.9	90.2
CONV. OF 600°F+	44.6	42.4	59.5	55.1	54.7	55.8	69.2	71.8	86.1	85.1
TOTAL CONV., WT%										
to C <sub>5</sub> -400°F, WT%	13.9	11.8	19.8	19.8	18.5	19.5	23.2	25.3	31.5	30.6
VOL%	17.0	14.5	24.2	24.2	22.7	23.9	28.4	30.9	38.5	37.4
SELECTIVITY	0.41	0.37	0.42	0.46	0.43	0.45	0.42	0.44	.45	.44
to 400-600°F, WT%	17.2	16.0	20.2	19.1	18.1	18.4	23.2	22.1	19.7	20.7
VOL%	19.1	17.8	22.4	21.2	20.0	20.4	25.7	24.5	21.9	22.9
SELECTIVITY	0.46	0.45	0.39	0.40	0.38	0.38	0.38	0.35	.26	.27
to C <sub>4</sub> MINUS GAS, WT%	8.1	9.0	13.0	11.5	10.1	9.9	13.8	15.0	22.3	21.8
*(GAS, WT% FEED)	10.3	10.4	17.6	16.1	12.9	14.3	17.7	20.3	25.7	25.4
*(GAS, WT% RECOVERY)	10.7	10.7	18.3	16.1	13.7	14.3	19.4	21.3	28.6	28.2
to COKE, WT%	5.4	5.5	6.5	4.7	8.0	8.0	9.1	9.4	12.6	12.0
(WT% C on FEED)	5.2	5.4	6.2	4.8	7.6	7.9	8.3	9.0	11.3	10.9
(WT% C on RECOVERY)	5.4	5.5	6.5	4.7	8.0	8.0	9.1	9.4	12.6	12.0
UNCONVERTED 600°F+, WT%	55.4	57.6	40.5	44.9	45.3	44.2	30.8	28.2	13.9	14.9
UNCONVERTED 600°F+, VOL%	58.4	60.7	42.7	47.3	47.7	46.6	32.4	29.7	14.6	15.8
<u>PRODUCTS, WT% RECOVERY</u>										
C <sub>5</sub> - 600°F RECOVERED, VOL%	100	99.9	100	100	100	100	100.1	100	100	100
	36.1	31.3	46.6	45.4	42.7	44.3	54.1	55.4	60.4	60.3

Note: Conversions Determined on a Recovered Weight Bases  
\* Total Gas, Includes C<sub>5</sub>+ Components

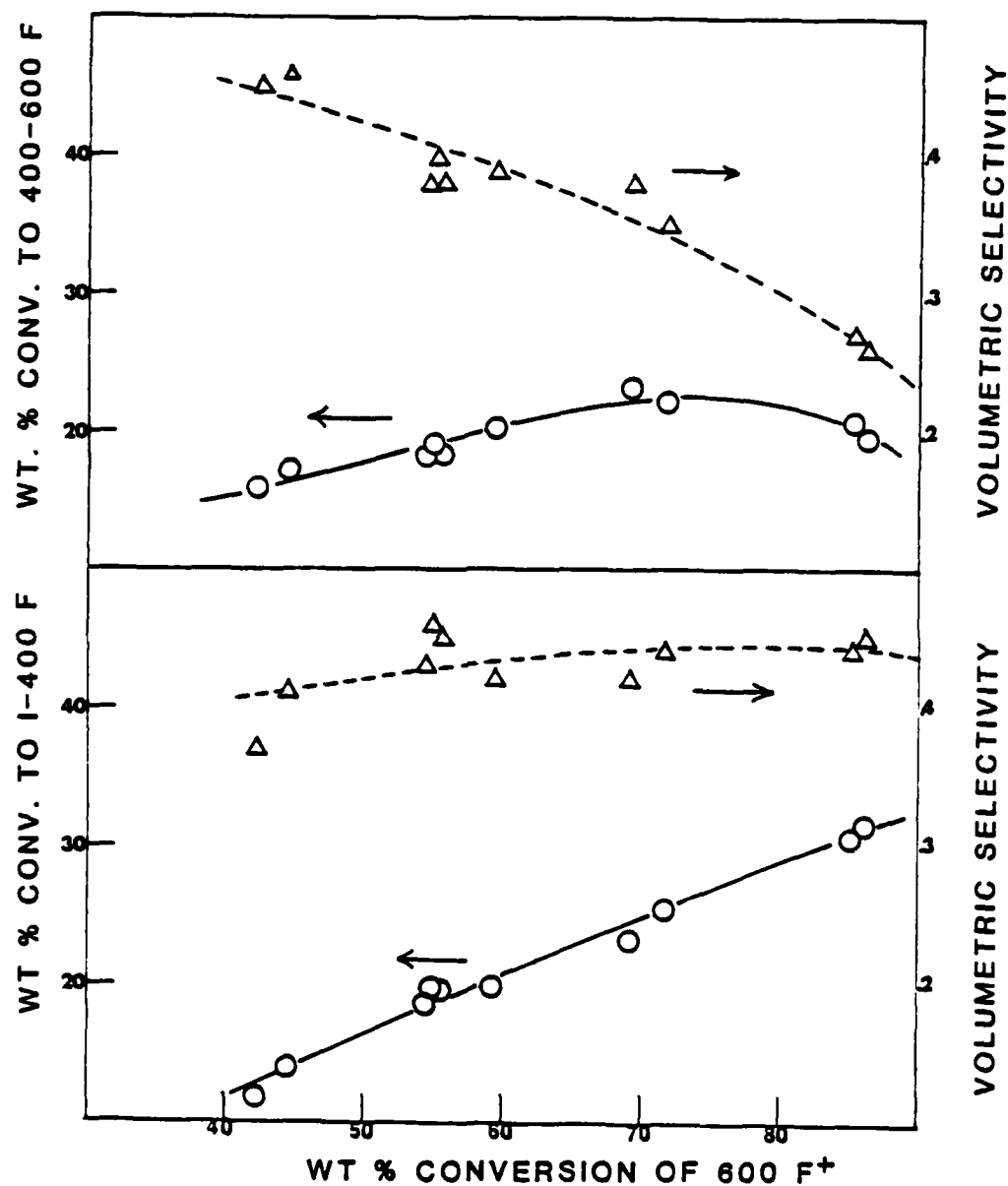


Figure IV-1. Microactivity Test Cracking  
Sample M212

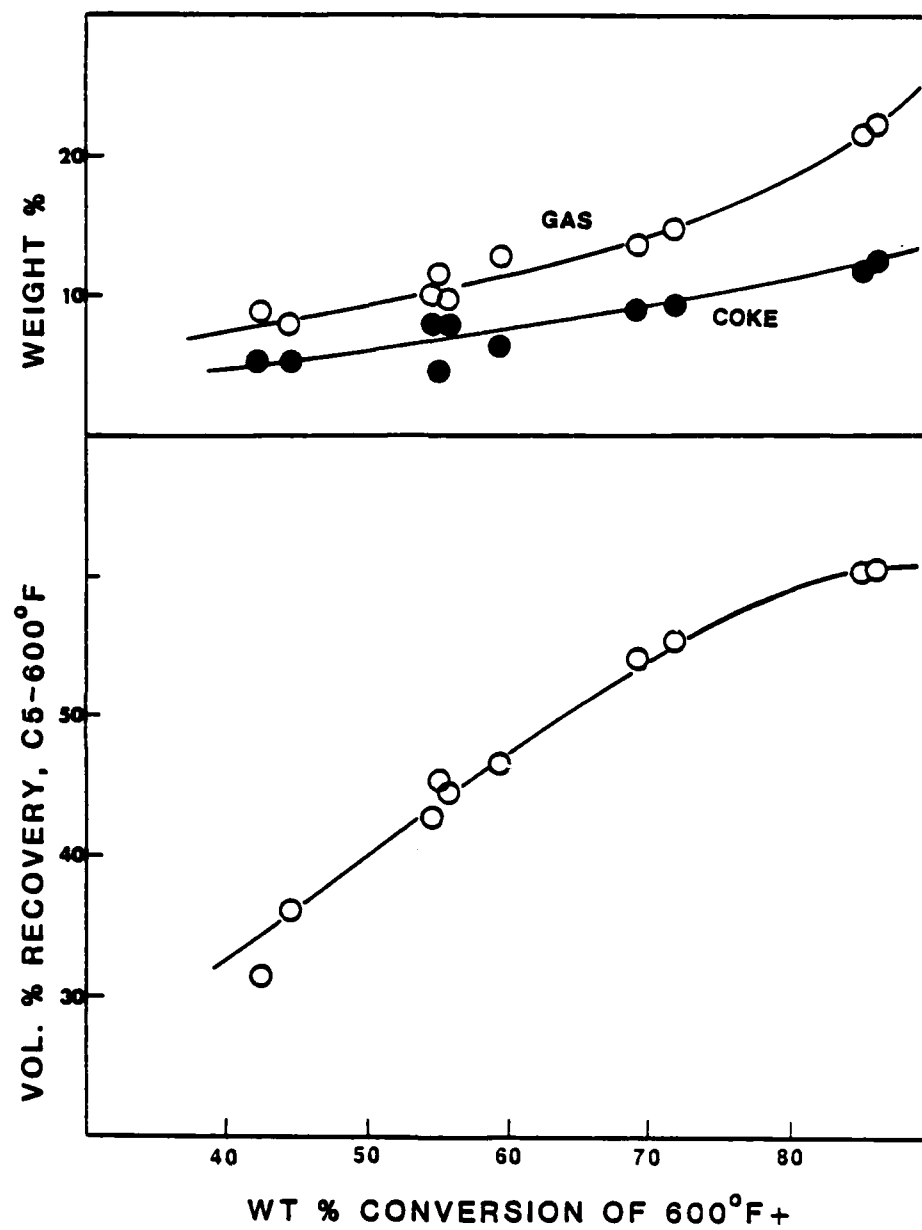


Figure IV-2. Microactivity Test Cracking  
Sample M-212

**TABLE IV-3**  
**PHASE II MAT SUMMARY - M221**

<u>RUN NO.</u>	<u>CATALYST/FEEDSTOCK</u>	<u>CONDITONS</u>	<u>TEMP., °F</u>	117	118	119	120	121	122	123	124	133	134
				950	950	1000	1000	950	950	1000	1000	1050	1050
				3.0	3.0	2.9	3.0	5.5	5.6	5.5	5.6	5.5	5.6
				15.5	15.5	16.0	15.5	8.7	8.6	8.8	8.5	8.7	8.6
				98.6	99.1	95.0	97.8	95.5	96.7	93.8	92.7	89.0	88.4
				43.3	33.8	49.4	53.1	50.5	52.4	65.4	65.9	84.3	82.8
				16.5	11.1	18.6	19.8	18.1	19.8	24.3	24.1	32.1	29.6
				20.1	13.5	22.6	24.1	22.0	24.0	29.5	29.3	39.0	35.9
				0.47	0.41	0.47	0.46	0.44	0.46	0.45	0.45	.46	.43
				13.9	11.3	16.3	16.8	15.4	15.6	18.9	19.9	17.4	18.4
				15.3	12.5	17.9	18.5	17.0	17.1	20.8	21.9	19.2	20.3
				0.36	0.38	0.37	0.35	0.34	0.33	0.32	0.34	.23	.25
				8.4	7.3	9.8	11.8	9.4	9.7	13.9	13.3	23.4	23.5
				10.9	9.5	12.6	15.9	13.0	14.6	18.1	17.0	27.0	26.0
				11.1	9.6	13.3	16.3	13.6	14.6	18.1	17.0	30.3	29.4
				4.4	4.0	4.7	4.6	7.4	7.3	8.2	8.7	11.3	11.3
				4.2	3.9	4.3	4.	6.9	6.9	7.5	7.7	9.8	9.7
				4.3	3.9	4.6	4.	7.2	7.1	8.0	8.4	11.0	11.0
				56.7	66.2	50.6	46.9	49.6	47.6	34.6	34.1	15.7	17.2
				59.3	69.2	53.0	49.1	51.9	49.8	36.2	35.7	16.4	18.0
				99.9	99.9	100	99.9	99.9	100	99.9	100.1	99.9	100
				35.4	26.0	40.5	42.6	39.0	41.1	50.3	51.2	58.2	56.2

Note: Conversions Determined on a Recovered Weight Bases  
\* Total Gas, Includes C<sub>5</sub>+ Components

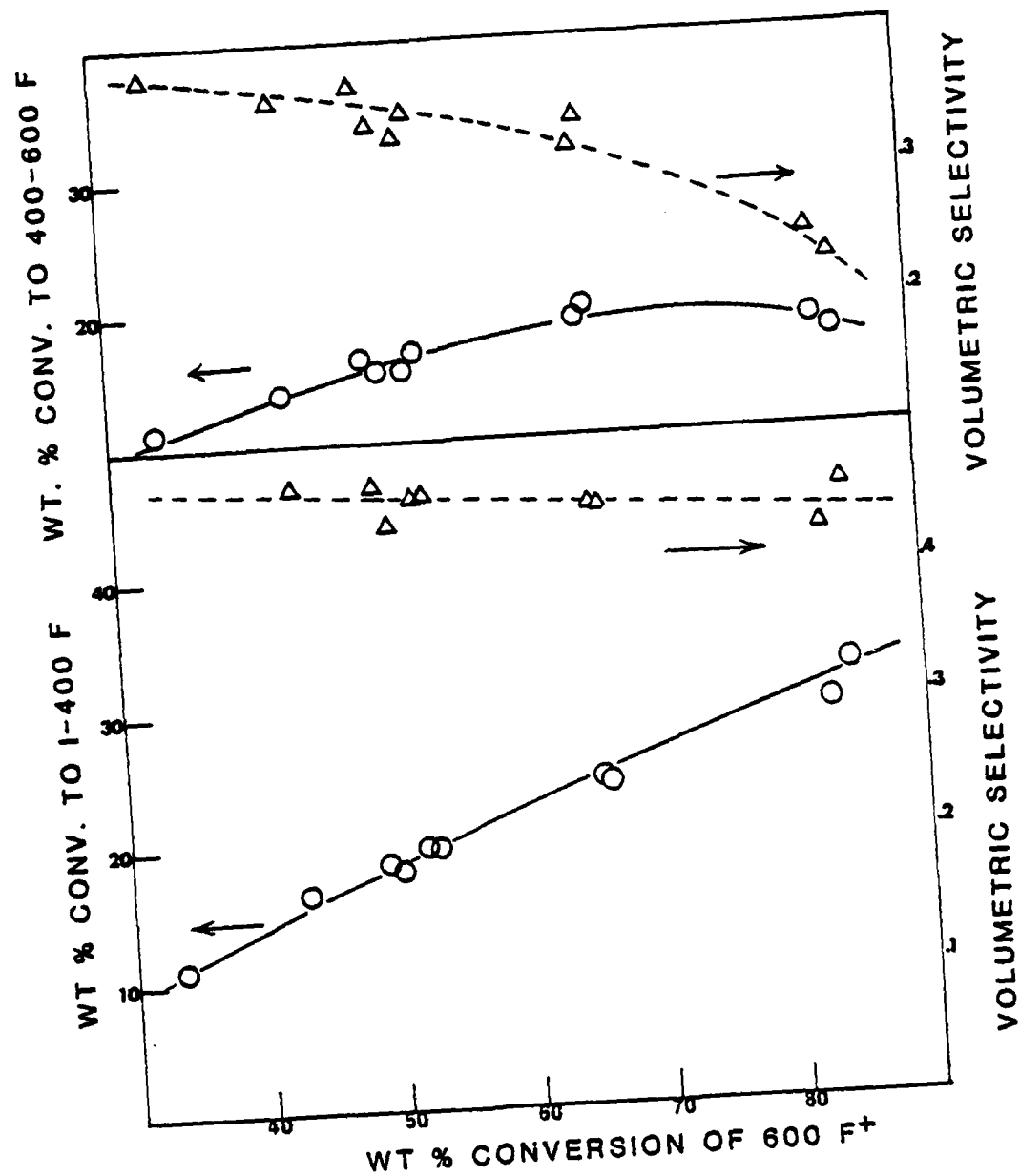


Figure IV-3. Microactivity Test Cracking  
Sample M221

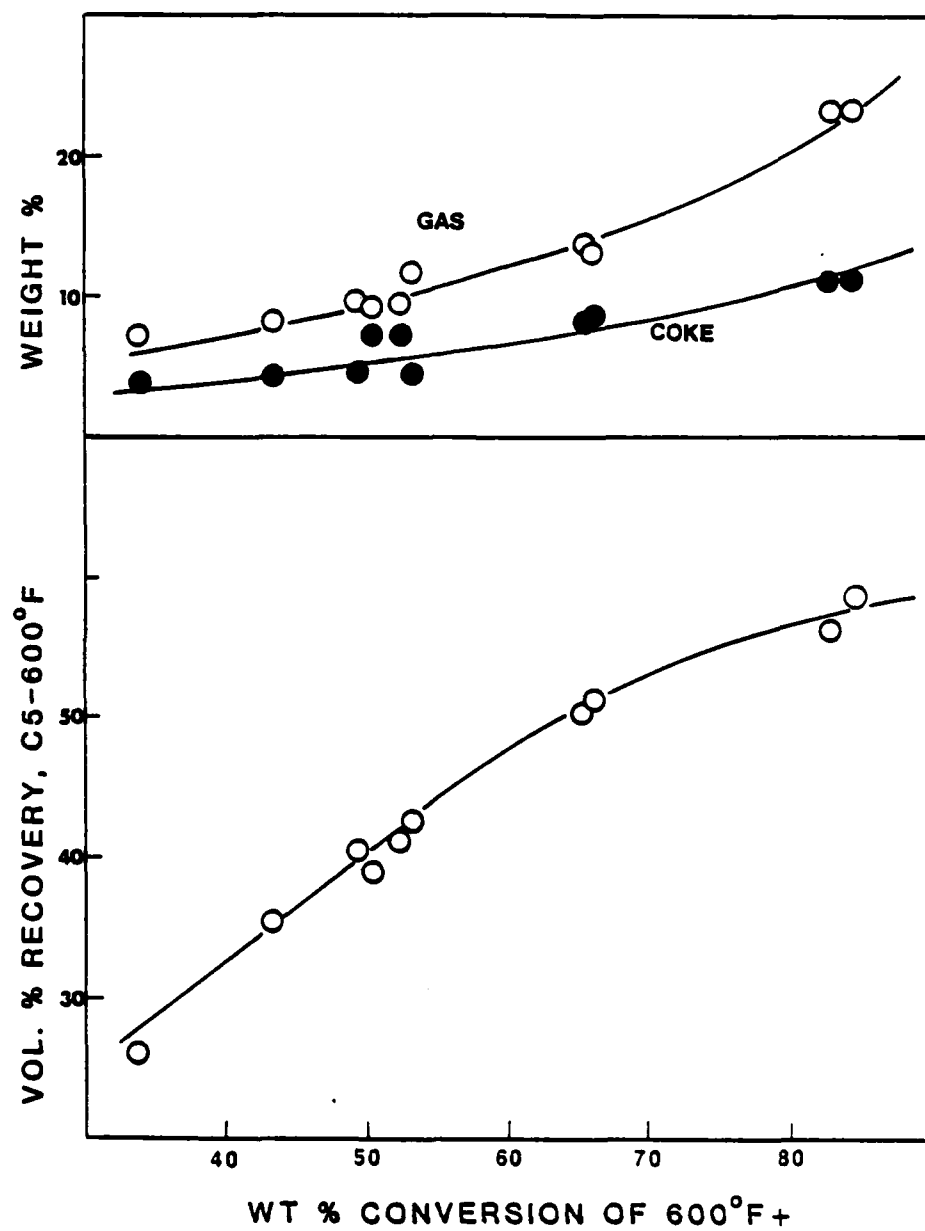


Figure IV-4. Microactivity Test Cracking  
Sample M-221

**TABLE IV-4**  
**PHASE II MAT SUMMARY-2135**

<u>RUN-NO.</u>	<u>152</u>	<u>153</u>	<u>154</u>	<u>155</u>	<u>156</u>	<u>157</u>	<u>158</u>	<u>160</u>	<u>161</u>
<u>CATALYST/FEEDSTOCK</u>									
<u>CONDITIONS</u>									
TEMP., °F	950	950	1000	1000	950	950	1000	1050	1050
CAT./OIL	3.0	2.9	3.1	3.1	5.2	5.6	5.8	5.8	6.0
WHSV	15.5	15.9	15.3	15.1	8.9	8.6	8.3	8.3	8.1
<u>TEST RESULTS</u>									
RECOVERY, WT%	93.3	96.1	99.5	99.9	95.8	90.8	92.0	93.3	86.7
CONVERSION OF 600°F ±									
TOTAL CONV., WT%	35.1	32.6	45.7	48.5	53.3	59.1	66.4	82.3	78.3
to C <sub>5</sub> -400°F, WT%	17.9	16.5	22.2	22.7	26.9	31.2	32.6	37.7	35.5
VOL. %	20.7	19.0	25.6	26.2	31.0	36.0	37.6	53.5	41.0
SELECTIVITY	.46	.44	.47	.47	.51	.55	.53	.51	.50
to 400-600°F, WT%	3.1	4.1	5.7	6.7	5.2	7.0	6.4	4.6	6.0
VOL. %	3.2	4.3	5.9	7.0	5.5	7.3	6.7	5.8	6.3
SELECTIVITY	.07	.10	.11	.12	.09	.11	.09	.07	.08
to C <sub>4</sub> MINUS GAS, WT%	10.6	9.1	14.4	15.7	14.2	14.3	20.6	31.7	29.3
*(GAS, WT% FEED)	14.6	12.8	20.2	21.0	19.6	18.1	24.6	36.7	31.7
*(GAS, WT% RECOVERY)	15.6	13.3	20.3	21.1	20.5	20.0	26.7	39.3	36.5
to COKE, WT%	3.5	3.0	3.4	3.4	7.0	6.7	6.8	7.4	7.4
(WT% C on FEED)	2.8	2.5	2.9	2.9	5.7	5.2	5.3	5.9	5.5
(WT% C on RECOVERY)	3.0	2.6	2.9	2.9	6.0	5.7	5.8	6.3	6.3
UNCONVERTED 600°F±, WT%	64.9	67.4	54.3	51.5	46.7	40.9	33.6	17.7	21.7
UNCONVERTED 600°F±, VOL%	64.5	67.0	54.0	51.2	46.5	40.6	33.4	17.6	21.6
± PRODUCTS, WT% RECOVERY	100.0	100.1	100.00	100.00	100.00	100.1	100.0	100.1	99.9
C <sub>5</sub> - 600°F RECOVERED, VOL%	23.9	23.3	31.5	33.2	36.5	43.3	44.3	49.3	47.3



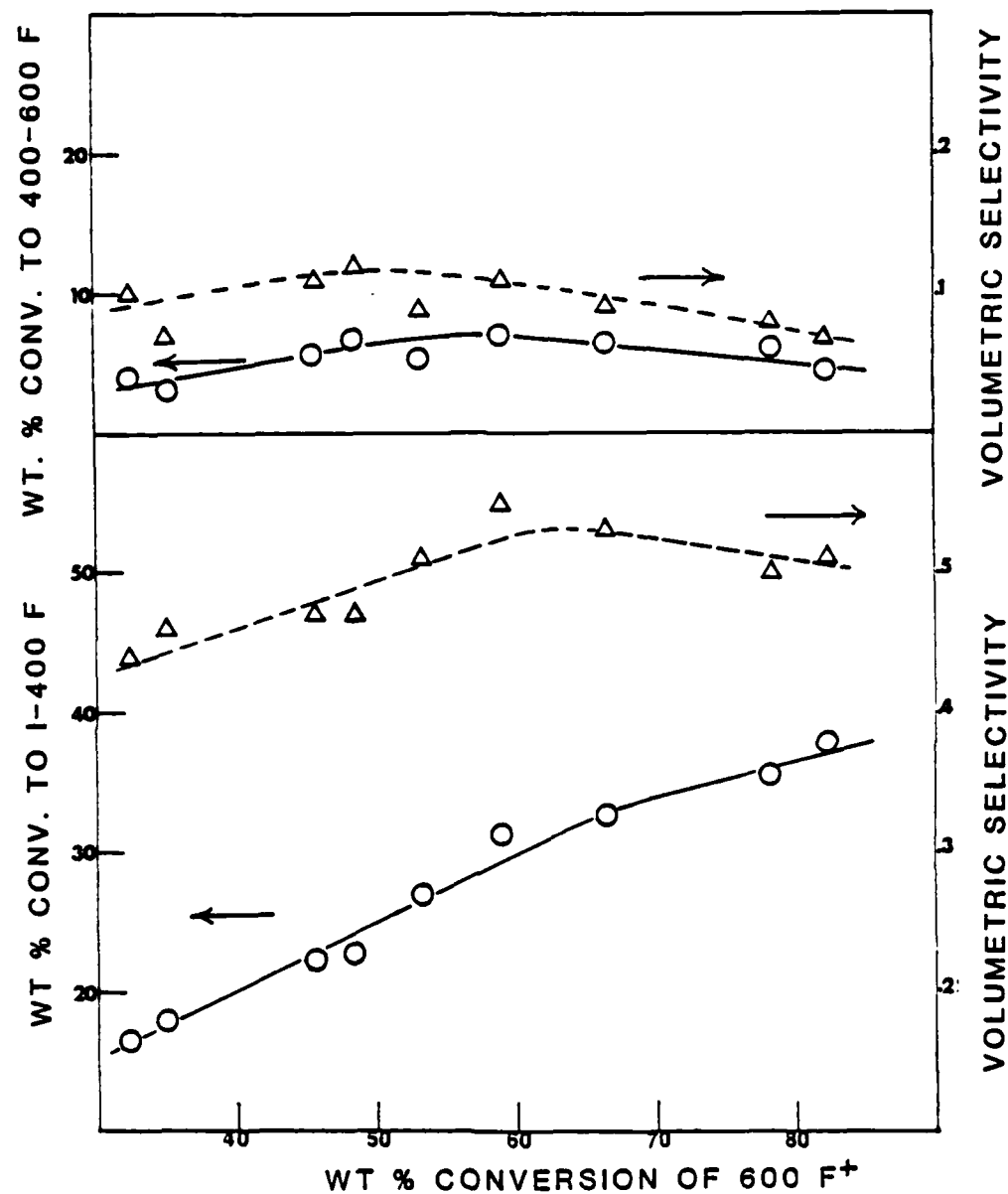


Figure IV-5. Microactivity Test Cracking  
Sample 2135

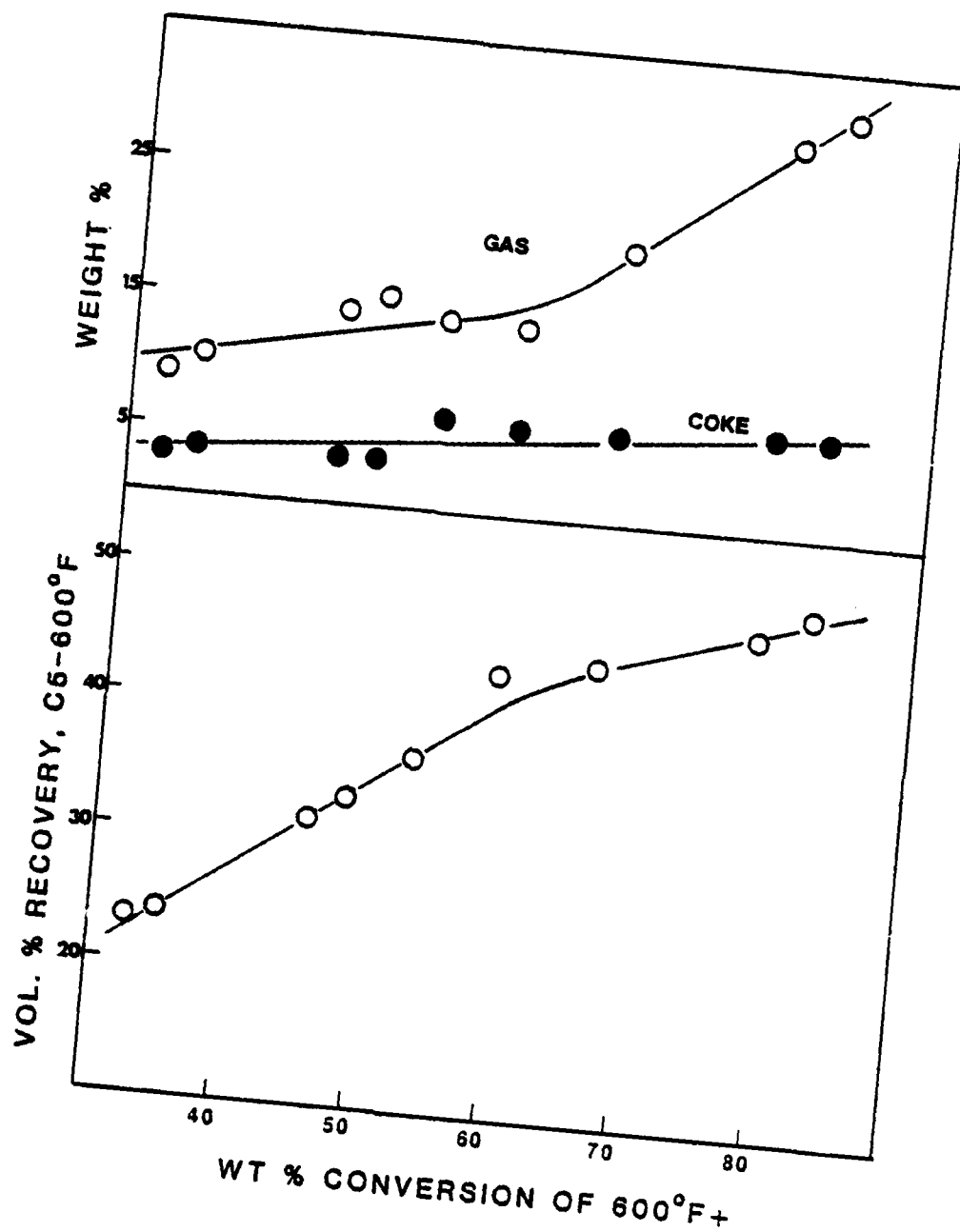


Figure IV-6. Microactivity Test Cracking  
Sample 2135

severity hydrotreating produced better cracking results, particularly in terms of coke production. Relatively high gas makes were produced during all runs, and the maximum C<sub>5</sub>-400°F fraction yields were somewhat lower than had been expected.

### CONCLUSIONS

An acceptable range of conversions can be attained for above-ground hydrotreated shale oil.

### 2. FCR PROCESSING - M SERIES (FRESH FEED)

### SUMMARY

A circulating fluidized bed catalytic cracking pilot plant was utilized to catalytically crack, under specified conditions, nominal five gallon samples of various qualities hydrotreated shale oil fractions. Full product yields and quality parameters were measured and adequate quantities of product collected for further processing. Successful processing on an integrated fluid cracking unit was demonstrated.

### OBJECTIVES

Objectives for these studies were to: (1) demonstrate the validity of concurrently-developed microactivity test data, (2) produce adequate quantities of material for further processing and (3) determine detailed product quality characteristics for varying feedstocks.

#### MECHANICAL DESCRIPTION

The R&D fluid catalytic reactor (FCR) is a miniature version of full-scale operating FCC units. Specific details of the unit are proprietary, but in general, the unit is composed of riser, catalyst disengaging and stripping, regeneration, and regenerated catalyst standpipe. Regenerated catalyst is metered to the riser where it is admixed with oil feed by means of a slide valve. The catalyst/oil mixture flows in dilute phase to the catalyst disengaging section where the catalyst and product vapors are separated, effectively terminating the reaction. Residual oil content is minimized in the stripping section and the stripped catalyst returned to the regenerator. Carbon content of the spent, stripped catalyst is removed by air combustion in the regenerator and the catalyst returned to the regenerated catalyst standpipe for reuse.

Catalyst inventory and circulation rates are such that the unit can be operated over varying time periods. The unit, due to its small size, is not heat balanced, being provided with external electrical resistance heaters on automatic temperature control. Product vapors are condensed and collected, with product fractionation offline. All flows are measured to provide material balance capabilities and control for the system. Regenerator flue gas composition, spent catalyst carbon content and regenerated catalyst content are monitored for material balance purposes as well.

The unit has been developed over an extensive number of petroleum feedstocks and has been demonstrated to produce results correlatable to that obtained in commercial operations.

#### FEEDSTOCK

Three above-ground source feedstocks were used in this study. Sample M-211 was produced in crude shale hydro-treater run M-21 over cobalt molybdate catalyst. The total hydrotreater product was fractionated to a 500°F nominal overhead temperature, with the 500°F+ bottoms product provided to the FCR for processing. Sample M-212 was produced from the same hydrotreating study as M-211, but the fractionation was performed to a 600°F cut point instead of 500°F. Finally, sample M-221 was produced in an analogous manner, but over nickel molybdate catalyst and fractionated to a 600°F cut point. Properties of each feed are shown in the results table for each FCR run.

#### EXPERIMENTAL

One charge of equilibrium zeolite FCC catalyst, obtained from Ashland's petroleum refining operations, was used for all evaluations. Two three-hour material balance periods were performed for each sample.

Operations were smooth in all cases, although some catalyst flow stability problems were encountered, and good material balance closures obtained. During each run product gas samples, regenerator flue gas samples, spent and

regenerated catalyst samples and composite liquid product samples were collected and analyzed.

The remaining composite liquid samples were collected in five-gallon cans, batch fractionated and analyzed. The distillate product portion was supplied for further processing by extraction and the heavy liquid product retained for further upgrading studies.

### RESULTS

Tables IV-5, IV-6 and IV-7 summarize results for these samples. Conversion of M-211 is based on the 500°F+ portion of feed and product; conversion of M-212 and M-221 is based on the 600°F+ portion of feed and product.

### DISCUSSION

Mechanical limitations during these runs were encountered which hampered accurate evaluations of these materials as feedstock to a commercial FCC unit. First, during processing of Sample M-211, regenerator limitations resulted in a high (0.52) carbon content on regenerated catalyst. This atypically high coke level on the feed catalyst would be expected to significantly diminish its activity, reducing desired distillate yields and yield quality and increasing coke production at equivalent operating severity. Second, catalyst flow rates were unable to be controlled at the desired catalyst-to-oil ratio, resulting in relatively high treatment rates.

TABLE IV-5

**FLUID CATALYTIC CRACKING  
ECR PROCESSING - SAMPLE M211**

Operating Conditions		Liquid Properties				
		Item	Feed	Total Product	- 500°F <sup>b</sup>	+ 500°F
Temperature, °F	970	°API	21.6	26.9	-	23.0
Cat/Oil Ratio	19.4	Carbon, % <sub>w</sub>	86.0	-	-	-
C on Regen Cat, %	0.52	Hydrogen, % <sub>w</sub>	10.88	-	-	-
Conversion, Wt % <sup>a</sup>	40.5	Nitrogen, % <sub>w</sub>	(2.05)	(1.245)	-	(1.646)
Closure, Wt %	99.1	N <sub>basic</sub> , % <sub>w</sub>	1.266	-	-	-
		Sulfur, % <sub>w</sub>	0.26	0.14	-	0.18
		Oxygen, % <sub>w</sub>	-	-	-	-
		Rams C, % <sub>w</sub>	1.18	-	-	1.20
		Aromatics, % <sub>w</sub>	-	-	-	-
		GHV, Btu/lb	-	-	-	-
		Distillation, Wt % (°F) by D-2887			-	-
		IBP	515	159	-	439
		2	529	209	-	475
		10	577	339	-	537
		30	685	545	-	612
		50	781	632	-	688
		70	861	732	-	775
		90	951	854	-	885
		98	998	934	-	968
		EP	1010	957	-	1003
Product Yields, Wt %						
		H <sub>2</sub>	0.23			
		C <sub>1</sub>	0.54			
		C <sub>2</sub>	1.47			
		C <sub>3</sub>	0.57			
		C <sub>3</sub> <sup>=</sup>	1.27			
		iC <sub>4</sub>	0.19			
		nC <sub>4</sub>	0.25			
		C <sub>4</sub> <sup>=</sup>	1.32			
		C <sub>5</sub> - 500	17.30			
		500+	59.9			
		Coke	16.92			

a - Based on the 500 °F point  
( ) - Calculated  
b - Data not available

TABLE IV-6

# FLUID CATALYTIC CRACKING FCR PROCESSING - SAMPLE M212

Operating Conditions		Liquid Properties				
		Item	Feed	Total Product	- 600°F	+ 600°F
Temperature, °F	1009	°API	19.7	25.8	40.7	18.4
Cat/Oil Ratio	10.6	Carbon, % <sub>w</sub>	87.2	-	-	-
C on Regen Cat, %	0.05	Hydrogen, % <sub>w</sub>	10.9	-	12.1	-
Conversion, Wt % <sup>a</sup>	52.2	Nitrogen, % <sub>w</sub>	(2.10)	(1.329)	(1.335)	(2.046)
Closure, Wt %	99.3	N <sub>basic</sub> , % <sub>w</sub>	1.338	-	0.779	-
		Sulfur, % <sub>w</sub>	0.24	0.19	0.15	0.22
		Oxygen, % <sub>w</sub>	-	-	-	0.231
		Rams C, % <sub>w</sub>	1.42	-	-	1.83
		Aromatics, % <sub>w</sub>	-	-	-	-
		GHV, Btu/lb	-	-	-	-
		Distillation, Wt % (°F) by D-2887	-	-	-	-
		IBP	569	126	120	492
		2	611	187	149	546
		10	666	305	217	634
		30	754	542	307	698
		50	829	679	380	762
		70	897	775	451	833
		90	985	891	532	921
		98	1017	987	603	980
		EP	1020	1017	660	995
Product Yields, Wt %						
		H <sub>2</sub>	0.25			
		C <sub>1</sub>	0.89			
		C <sub>2</sub>	1.93			
		C <sub>3</sub>	0.79			
		C <sub>3</sub> <sup>m</sup>	2.10			
		iC <sub>4</sub>	0.34			
		nC <sub>4</sub>	0.41			
		C <sub>4</sub> <sup>m</sup>	2.53			
		C <sub>5</sub> - 600	28.80			
		600+	48.08			
		Coke	13.88			

<sup>a</sup> - Based on the 600 °F point

( ) - Calculated



TABLE IV-7

# FLUID CATALYTIC CRACKING FCR PROCESSING - SAMPLE M221

Operating Conditions		Liquid Properties				
		Item	Feed	Total Product	- 600°F	+ 600°F
Temperature, °F	1007	°API	20.9	27.1	42.4	19.6
Cat/Oil Ratio	17.8	Carbon, % <sub>w</sub>	87.5	-	-	-
C on Regen Cat, %	0.01	Hydrogen, % <sub>w</sub>	10.1	-	12.2	-
Conversion, Wt % <sup>a</sup>	62.9	Nitrogen, % <sub>w</sub>	(2.065)	(1.370)	(1.183)	(1.828)
Closure, Wt %	98.7	N <sub>basic</sub> , % <sub>w</sub>	1.311	-	0.741	-
		Sulfur, % <sub>w</sub>	0.15	0.16	0.15	0.17
		Oxygen, % <sub>w</sub>	-	-	-	0.197
		Rams C, % <sub>w</sub>	1.04	-	-	2.04
		Aromatics, % <sub>w</sub>	-	-	-	-
		GHV, Btu/lb	-	-	-	-
		Distillation, Wt % (°F) by D-2887	-	-	-	-
		IBP	594	122	133	491
		2	600	169	148	531
		10	640	282	209	601
		30	725	480	284	662
		50	804	629	343	723
		70	873	721	414	797
		90	958	846	520	892
		98	1001	930	590	963
		EP	1013	956	620	999
Product Yields, Wt %						
		H <sub>2</sub>	0.22			
		C <sub>1</sub>	0.88			
		C <sub>2</sub>	1.96			
		C <sub>3</sub>	0.70			
		C <sub>3</sub> <sup>=</sup>	2.22			
		iC <sub>4</sub>	0.36			
		nC <sub>4</sub>	0.35			
		C <sub>4</sub> <sup>=</sup>	2.66			
		C <sub>5</sub> - 600	33.66			
		600 +	37.38			
		Coke	19.61			

<sup>a</sup> - Based on the 600 °F point

( ) - Calculated

This type of high treatment rate, for the high basic nitrogen shale oil feedstocks in particular, will result in analogously high coke production due to physical interactions between the basic nitrogen species and the acidic catalyst sites.

Irrespective of these problems, conversions were attained ranging from 40 to 63 weight percent based on the feed's cut points. While coke production in all cases was excessive, the M-212 run demonstrates the positive impact of both reducing regenerated catalyst carbon level and reducing the imposed catalyst-to-oil ratio.

Of particular importance in the results presented in Tables IV-5, IV-6 and IV-7, relatively high levels of denitrogenation were obtained for all samples. Denitrogenation for the samples, based only on feed versus whole liquid product, ranged from 34 to 39 percent, while desulfurization ranged from an apparent zero to 49 percent. Based on the very limited oxygen data available, there was no readily apparent significant deoxygenation of these materials.

Data for samples M-212 and M-221 also demonstrate a key aspect of FCC processing in general. While feedstock hydrogen content was 10.9 and 10.1 weight percent, respectively, the produced distillate material demonstrated hydrogen contents of 12.1 and 12.2 percent, respectively, without external hydrogen addition. In simplistic terms, this

corresponds to an increase in stream hydrogen content of 10 to 20 percent, or on the order of addition of 500 to 1000 SCFB of external hydrogen.

#### RECOMMENDATIONS AND CONCLUSIONS

- Higher than desired catalyst-to-oil ratios were encountered in all cases, and in one case excessively high carbon on regenerated catalyst was also present.
- Higher coke yields, and somewhat lower distillate yields, were encountered than expected.
- Significant levels of denitrogenation were attained; desulfurization was attained in two of the three cases.
- Very high hydrogen redistribution was demonstrated.
- Adequate products for further processing were produced.
- Detailed product qualities were developed.

#### 3. FCR PROCESSING - PHO SAMPLE (FRESH FEED)

##### SUMMARY

A circulating fluidized bed catalytic cracking pilot plant was utilized to catalytically crack, under specified conditions, nominal five gallons of various qualities of shale oil feedstock. Full product yields and quality parameters were measured and adequate quantities of product collected for further processing. Successful processing on an integrated fluid cracking unit was demonstrated.

### OBJECTIVES

Objectives for these studies were to: (1) demonstrate the validity of concurrently-developed microactivity test data, (2) produce adequate quantities of material for further processing and (3) determine detailed product quality characteristics. These objectives are analogous to those delineated in Part 2 for the M-Series samples. Further objectives for these samples, however, were provided by: (1) evaluating the effect of feeding full-range crude shale hydrotreater product and (2) examining a series of samples from the hydrotreater aging studies to determine the impacts of hydrotreater catalyst age on fluid cracking results.

### EXPERIMENTAL

Experimental procedures for each of these runs were analogous to those utilized during the M-Series studies (Part 2). These runs were again relatively smooth, with reasonable material balance closures obtained in each case. Material balance period's ranges were 4 to 5 hours each.

Sampling was also practiced in a manner analogous to the FCR M-Series runs. Each product composite was again fractionated  $\pm 600^{\circ}\text{F}$ , evaluated and utilized for further processing.

### MECHANICAL DESCRIPTION

The equipment and catalyst utilized are analogous to that described in Part 2 for the M-Series samples.

### FEEDSTOCK

Above-ground feedstocks for these runs were composite products from the previously described hydrotreater aging runs (Section III, Part 3). Material composites from hydrotreater aging periods 1-4 (PHO-1), 10-12 (PHO-2), 18-20 (PHO-3), and 26-27 (PHO-4) were stabilized to 125°F atmospheric overhead temperature and provided to the FCR operators as a full range, rather than fractionated, feedstock. Properties of these feedstocks are shown in Tables IV-8 through IV-11, as well as in Section III.

### RESULTS

Results from these runs are shown in Tables IV-8 through IV-11.

### DISCUSSION

These runs were the first in which full-range hydro-treated above-ground shale oil was charged to the cracker in an effort to take advantage of both the heteroatom removal capability of the unit, as well as to obtain the previously encountered improvement in extractability of the distillate product. Conversions ranged from 37 to 52 weight percent based on 600°F. Analogous operations during the M-Series studies had shown conversions ranging from 40 to 63 percent, but for the most part these studies were comparable at similar conditions. Yields were observed to be marginally lowered.

TABLE IV-8

# FLUID CATALYTIC CRACKING FOR PROCESSING - SAMPLE PHO-1

Operating Conditions		Liquid Properties				
		Item	Feed	Total Product	- 600°F	+ 600°F
Temperature, °F	1000	°API	23.9	29.1	36.9	21.2
Cat/Oil Ratio	9.65	Carbon, % <sub>w</sub>	-	-	-	-
C on Regen Cat, %	0.13	Hydrogen, % <sub>w</sub>	-	-	12.73	11.29
Conversion, Wt % <sup>a</sup>	37.13	Nitrogen, % <sub>w</sub>	(2.01)	-	1.20	1.87
Closure, Wt %	89.0	Nbasic, % <sub>w</sub>	(1.28)	-	0.928	0.767
		Sulfur, % <sub>w</sub>	(0.19)	-	0.18	0.18
		Oxygen, % <sub>w</sub>	-	-	-	-
		Rams C, % <sub>w</sub>	(1.50)	-	-	1.27
		Aromatics, % <sub>w</sub>	-	-	-	55.1
		GHV, Btu/lb	-	-	-	-
		Distillation, Wt % (°F) by D-2887	-	-	-	-
		IBP	317	-	-	-
		2	356	-	-	-
		10	451	-	-	-
		30	599	-	-	-
		50	725	-	-	-
		70	833	-	-	-
		90	942	-	-	-
		98	996	-	-	-
		EP	1010	-	-	-
Product Yields, Wt %		H <sub>2</sub>	0.23			
		C <sub>1</sub>	0.43			
		C <sub>2</sub>	1.13			
		C <sub>3</sub>	0.67			
		C <sub>3</sub> <sup>=</sup>	1.37			
		iC <sub>4</sub>	0.25			
		nC <sub>4</sub>	0.34			
		C <sub>4</sub> <sup>=</sup>	1.72			
		C <sub>5</sub> - 600	37.16			
		600 +	43.82			
		Coke	12.65			

<sup>a</sup> - Based on the 600 °F point

( ) Calculated

TABLE IV-9

# FLUID CATALYTIC CRACKING FCC PROCESSING - SAMPLE PHO-2

Operating Conditions		Liquid Properties				
		Item	Feed	Total Product	- 600°F	+ 600°F
Temperature, °F	1017	°API	25.1	31.2	38.5	21.7
Cat/Oil Ratio	10.29	Carbon, % <sub>w</sub>	-	-	-	-
C on Regen Cat, %	0.16	Hydrogen, % <sub>w</sub>	-	-	12.45	11.32
Conversion, Wt % <sup>a</sup>	48.81	Nitrogen, % <sub>w</sub>	2.07	-	(1.11)	(1.53)
Closure, Wt %	93.4	N <sub>basic</sub> , % <sub>w</sub>	1.30	-	0.776	0.660
Product Yields, Wt %		Sulfur, % <sub>w</sub>	0.21	-	0.10	0.10
		Oxygen, % <sub>w</sub>	-	-	-	-
		Rams C, % <sub>w</sub>	1.61	-	-	1.87
		Aromatics, % <sub>w</sub>	-	-	-	54.4
		GHV, Btu/lb	-	-	-	-
		Distillation, Wt % (°F) by D-2887				
		IBP	319	-	-	-
		2	357	-	-	-
		10	452	-	-	-
		30	601	-	-	-
		50	728	-	-	-
		70	836	-	-	-
		90	943	-	-	-
		98	996	-	-	-
		EP	1010	-	-	-
		H <sub>2</sub>	0.27			
		C <sub>1</sub>	0.68			
		C <sub>2</sub>	1.14			
		C <sub>3</sub>	0.64			
		C <sub>3</sub> <sup>=</sup>	1.47			
		iC <sub>4</sub>	0.26			
		nC <sub>4</sub>	0.34			
		C <sub>4</sub> <sup>=</sup>	1.81			
		C <sub>5</sub> - 600	35.87			
		600 +	42.63			
		Coke	14.61			

<sup>a</sup> - Based on the 600 °F point

( ) Calculated

TABLE IV-10

# FLUID CATALYTIC CRACKING FCR PROCESSING - SAMPLE PHO-3

Operating Conditions		Liquid Properties				
		Item	Feed	Total Product	- 600°F	+ 600°F
Temperature, °F	980	°API	23.4	29.4	36.7	19.8
Cat/Oil Ratio	11.5	Carbon, % <sub>w</sub>	-	-	-	-
C on Regen Cat, %	0.01	Hydrogen, % <sub>w</sub>	-	-	12.44	-
Conversion, Wt % <sup>a</sup>	39.28	Nitrogen, % <sub>w</sub>	2.13	-	(1.61)	(1.81)
Closure, Wt %	79.5	Nbasic, % <sub>w</sub>	1.31	-	0.822	0.744
		Sulfur, % <sub>w</sub>	0.24	-	0.17	0.19
		Oxygen, % <sub>w</sub>	-	-	-	-
		Rams C, % <sub>w</sub>	1.70	-	-	1.99
		Aromatics, % <sub>w</sub>	-	-	-	-
		GHV, Btu/lb	-	-	-	-
		Distillation, Wt % (°F) by D-2887				
		IBP				
		2				
		10				
		30				
		50				
		70				
		90				
		98				
		EP				
Product Yields, Wt %						
		H <sub>2</sub>	0.18			
		C <sub>1</sub>	0.28			
		C <sub>2</sub>	0.44			
		C <sub>3</sub>	0.17			
		C <sub>3</sub> <sup>m</sup>	0.37			
		iC <sub>4</sub>	0.04			
		nC <sub>4</sub>	0.08			
		C <sub>4</sub> <sup>m</sup>	0.37			
		C <sub>5</sub> - 600	37.78			
		600 +	42.50			
		Coke	17.49			

<sup>a</sup> - Based on the 600°F point

( ) - Calculated



TABLE IV-11

**FLUID CATALYTIC CRACKING  
FCR PROCESSING - SAMPLE PHO-4**

Operating Conditions		Liquid Properties				
		Item	Feed	Total Product	- 600°F	+ 600°F
Temperature, °F	1005	°API	23.4	31.0	41.7	19.4
Cat/Oil Ratio	17.9	Carbon, % <sub>w</sub>	-	-	-	-
C on Regen Cat, %	0.18	Hydrogen, % <sub>w</sub>	-	-	12.43	-
Conversion, Wt % <sup>a</sup>	52.40	Nitrogen, % <sub>w</sub>	-	-	(1.39)	(1.83)
Closure, Wt %	98.9	N <sub>basic</sub> , % <sub>w</sub>	-	-	0.689	0.657
		Sulfur, % <sub>w</sub>	-	-	0.17	0.21
		Oxygen, % <sub>w</sub>	-	-	-	-
		Rams C, % <sub>w</sub>	-	-	-	2.56
		Aromatics, % <sub>w</sub>	-	-	-	-
		GHV, Btu/lb	-	-	-	-
		Distillation, Wt % (°F) by D-2887	-	-	-	-
		IBP	238	-	-	-
		2	310	-	-	-
		10	428	-	-	-
		30	581	-	-	-
		50	712	-	-	-
		70	831	-	-	-
		90	952	-	-	-
		98	1018	-	-	-
		EP	-	-	-	-
Product Yields, Wt %						
		H <sub>2</sub>	0.21			
		C <sub>1</sub>	0.72			
		C <sub>2</sub>	1.47			
		C <sub>3</sub>	0.56			
		C <sub>3</sub> <sup>=</sup>	1.78			
		iC <sub>4</sub>	0.27			
		nC <sub>4</sub>	0.30			
		C <sub>4</sub> <sup>=</sup>	2.18			
		C <sub>5</sub> - 600	42.05			
		600+	32.13			
		Coke	18.08			

<sup>a</sup> - Based on the 600 °F point

( ) - Calculated

Results from these runs demonstrate that full-range crude shale oil hydrotreater products can successfully be processed through the FCC unit. Overall yields, and yield quality, however, demonstrate that a significant penalty is imposed by processing the full-range hydrotreater product. Previously noted advantages, however, of selective hetero-atom removal and hydrogen redistribution were accomplished for these samples, as well. Again, these samples were later proven to be more amenable to extraction than the comparable mixed-feed (600°F+ charge to the cracker blended with hydrotreated straight-run distillate) operations.

#### RECOMMENDATIONS AND CONCLUSIONS

- Full range stocks are readily processed on the FCC unit.
- Products from full range cracking have less hetero-atoms and are more efficiently extracted than distillates which are a blend of cat cracked and straight run hydrotreated materials.
- Liquid yields, and in particular selective liquid yields (based on total distillate), suffer when charging a full-range feed to the FCC unit. Further, total gas production (hydrotreater plus FCC) is increased significantly by this mode of operation.

#### 4. MAT TESTS - RECYCLE

##### SUMMARY

FCC bottoms product, hydrotreated for recycle, has been evaluated over a range of conditions on the microactivity test unit. Conversions ranging 30 to 83 weight percent (600°F basis) were obtained for this material. The product distribution is significantly improved over the original fresh feed basis material as expected, with decreased coke, gas and distillate (400 to 600) yields, resulting in significantly increased C<sub>5</sub> to 400 and total distillate (C<sub>5</sub> to 600) at equivalent conversion levels when compared to the analogous fresh feed material. Data from this experimentation confirm the original yield structure projections for this type of recycle material.

##### OBJECTIVES

Objective for this study was to determine the yield structure response of hydrotreated recycle material in a rapid manner.

##### MECHANICAL DESCRIPTION

The equipment utilized for this study was identical to that used during Part 1, fresh feed studies.

##### EXPERIMENTAL

Experimental procedure was also analogous to that used in Part 1.

### FEEDSTOCK

The feedstocks utilized for these studies were stabilized product from the cycle oil hydrotreating studies (Section VI). Properties of these feedstocks and source identification data are shown in Tables VI-5 and VI-6 in Section VI.

### RESULTS

Tables IV-12 to IV-14 and Figures IV-7 to IV-12 present MAT results for the feedstocks processed.

### DISCUSSION

The three samples processed demonstrated a wide range of conversion in response to the conditions utilized. In particular, these materials demonstrated good selectivity to the lighter (C<sub>5</sub> to 400°F) liquid fractions. Good coke and reasonable gas production was attained, in particular for a recycle stock of this type.

### CONCLUSIONS

- Operating data over an appropriate range of conditions were derived for three recycle samples.

# TABLE IV-12

## PHASE II MAT SUMMARY M211 CO-HT 750°F, PERIOD 3

RUN NO. CONDITIONS TEMP., °F CAT./OIL WHSV	99		100		101		102		103		104		105		106		107		108	
	950	3.2	950	3.4	1000	3.2	1000	3.3	950	5.7	950	5.8	1000	5.8	1000	5.8	850	3.2	850	3.4
	14.6	14.6	13.6	13.6	14.5	14.5	14.3	7.9	7.9	7.9	7.8	7.8	7.8	7.8	7.8	7.8	14.7	14.7	13.6	13.6
TEST RESULTS																				
RECOVERY, WT%	99.5	99.5	99.5	99.5	95.9	95.9	95.8	99.0	99.0	101.1	101.1	95.9	98.3	97.6	101.1	97.6	101.1	97.6	101.1	101.1
CONV. OF 600°F+																				
TOTAL CONV., WT%	51.8	53.9	61.1	61.2	77.8	77.8	77.3	82.7	83.1	44.3	47.0	82.7	83.1	44.3	47.0	82.7	83.1	44.3	47.0	47.0
to C <sub>5</sub> -400°F, WT%	27.0	28.0	32.5	31.3	52.3	52.3	49.2	47.2	51.1	22.5	23.2	47.2	51.1	22.5	23.2	47.2	51.1	22.5	23.2	23.2
to C <sub>5</sub> -400°F, VOL%	31.1	32.3	37.4	36.0	60.3	60.3	56.6	54.4	58.8	26.0	26.7	54.4	58.8	26.0	26.7	54.4	58.8	26.0	26.7	26.7
SELECTIVITY	0.46	0.47	0.51	0.49	0.71	0.71	0.67	0.61	0.66	0.41	0.41	0.61	0.66	0.41	0.41	0.61	0.66	0.41	0.41	0.41
to 400-600°F, WT%	6.0	6.7	4.6	7.1	-3.7	-3.7	-3.8	-5.4	-5.6	11.2	10.7	-5.4	-5.6	11.2	10.7	-5.4	-5.6	11.2	10.7	10.7
to 400-600°F, VOL%	6.3	7.0	4.8	7.4	-3.8	-3.8	-4.0	-5.6	-5.9	11.7	11.2	-5.6	-5.9	11.7	11.2	-5.6	-5.9	11.7	11.2	11.2
SELECTIVITY	0.09	0.10	0.07	0.10	-0.05	-0.05	-0.05	-0.06	-0.07	0.19	0.17	-0.06	-0.07	0.19	0.17	-0.06	-0.07	0.19	0.17	0.17
to C <sub>4</sub> MINUS GAS, WT%	14.7	15.1	19.6	18.1	21.1	21.1	24.0	31.8	28.4	6.4	9.2	31.8	28.4	6.4	9.2	31.8	28.4	6.4	9.2	9.2
to C <sub>4</sub> MINUS GAS, WT% FEED	16.8	14.9	20.9	16.5	24.4	24.4	25.5	27.5	29.7	8.4	9.6	27.5	29.7	8.4	9.6	27.5	29.7	8.4	9.6	9.6
* (GAS, WT% RECOVERY)	16.8	15.0	21.9	17.2	24.6	24.6	25.2	28.7	30.3	8.6	9.5	28.7	30.3	8.6	9.5	28.7	30.3	8.6	9.5	9.5
to COKE, WT%	4.0	4.0	4.4	4.7	8.0	8.0	8.0	9.2	9.2	4.1	4.0	9.2	9.2	4.1	4.0	9.2	9.2	4.1	4.0	4.0
(WT% C on FEED)	2.7	2.7	2.9	3.0	5.4	5.4	5.4	5.9	6.1	2.7	2.7	5.9	6.1	2.7	2.7	5.9	6.1	2.7	2.7	2.7
(WT% C on RECOVERY)	2.7	2.7	3.0	3.2	5.4	5.4	5.4	6.2	6.2	2.8	2.7	6.2	6.2	2.8	2.7	6.2	6.2	2.8	2.7	2.7
UNCONVERTED 600°F+, WT%	48.2	46.1	38.9	38.8	22.2	22.2	22.7	17.3	16.9	55.7	53.0	17.3	16.9	55.7	53.0	17.3	16.9	55.7	53.0	53.0
UNCONVERTED 600°F+, VOL%	47.9	45.8	38.6	38.5	22.1	22.1	22.5	17.1	16.8	55.3	52.6	17.1	16.8	55.3	52.6	17.1	16.8	55.3	52.6	52.6
ΣPRODUCTS, WT% RECOVERY	99.9	99.9	100	100	99.9	99.9	100.1	100.1	100.1	99.9	100.1	100.1	100.1	99.9	100.1	100.1	99.9	100.1	100.1	100.1
C <sub>5</sub> - 600°F RECOVERED, VOL%	37.4	39.3	42.2	43.4	56.5	56.5	52.6	48.8	52.9	37.7	37.9	48.8	52.9	37.7	37.9	48.8	52.9	37.7	37.9	37.9

Note: Conversions Determined on a Recovered Weight Basis  
\* Total Gas, Includes C<sub>5</sub>+ Components

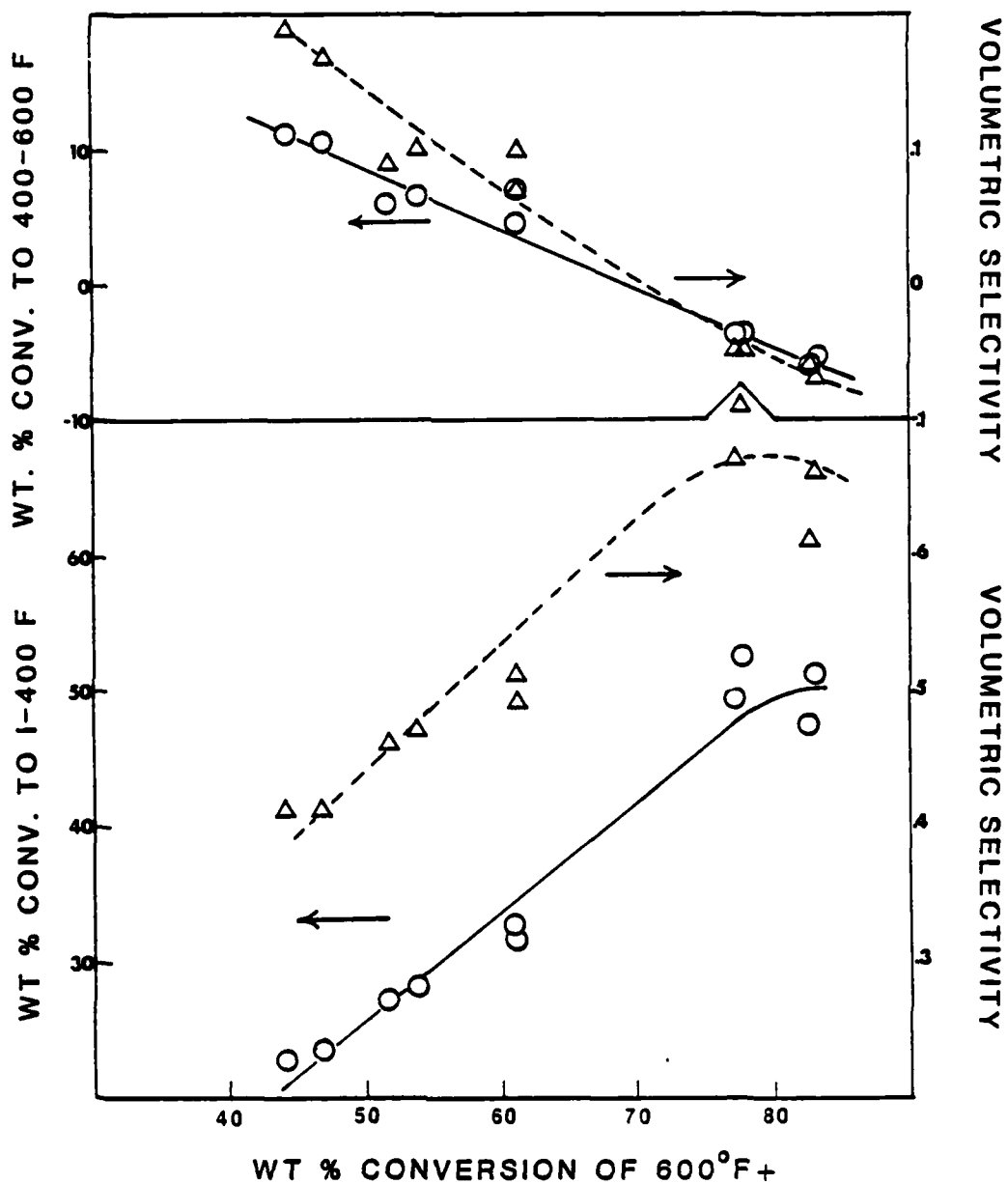


Figure IV-7. Microactivity Test Cracking  
Sample M211-LCO

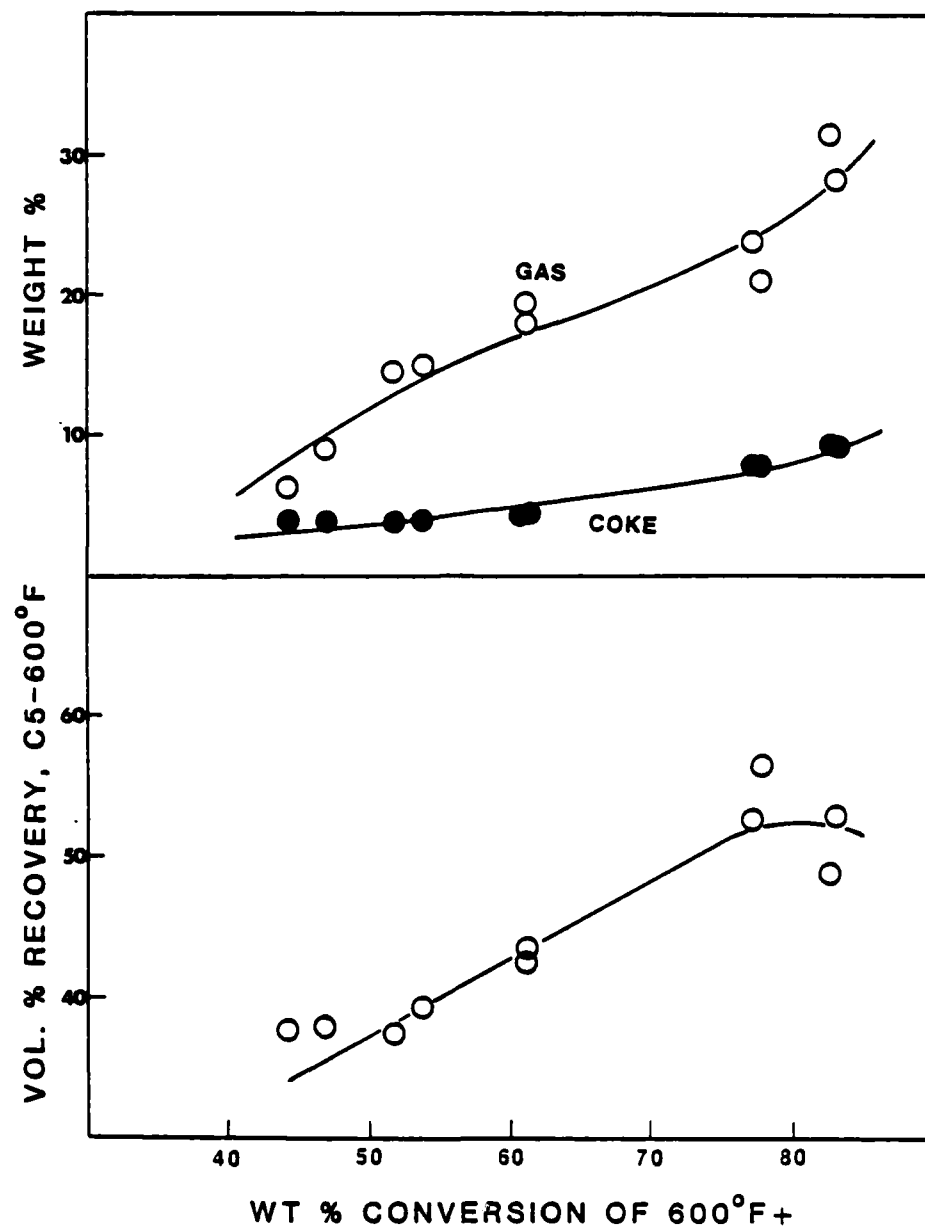


Figure IV-8. Microactivity Test Cracking  
Sample M211-LCO

# TABLE IV-13

## PHASE II MAT SUMMARY M212 CO-HT 700°F, PERIOD 5

RUN NO.	125	126	27	128	129	130	135	136	137	148	149
CONDITIONS											
TEMP., °F	950	950	1000	1000	950	950	1000	1000	1050	1050	1050
CAT./OIL	3.1	3.0	3.0	3.1	6.2	5.8	5.7	6.0	5.8	5.9	5.8
WHSV	15.3	15.7	15.5	15.3	7.7	8.3	8.5	8.0	8.3	8.1	8.1
TEST RESULTS											
RECOVERY, WT%	98.4	100.6	96.9	95.3	97.0	94.6	92.8	94.4	91.9	89.5	95.8
CONV. OF 600°F*	37.8	31.2	45.6	54.5	55.4	54.5	67.3	65.0	80.5	72.1	77.3
TOTAL CONV., WT%											
to C <sub>5</sub> -400°F, WT%	17.6	15.6	22.1	25.9	27.4	26.3	31.3	30.9	34.4	33.5	34.8
VOL%	20.9	18.5	26.2	30.7	32.5	31.2	37.1	36.7	40.8	39.7	41.3
SELECTIVITY	.43	.44	.48	.50	.52	.50	.51	.52	.49	.52	.51
to 400-600°F, WT%	5.5	3.9	6.7	6.4	5.8	5.7	8.0	5.6	5.3	6.4	5.0
VOL%	5.9	4.2	7.2	6.9	6.2	6.2	8.6	6.0	5.7	6.9	5.4
SELECTIVITY	.12	.10	.13	.11	.10	.10	.12	.08	.07	.09	.07
to C <sub>6</sub> MINUS GAS, WT%	11.3	9.1	12.7	18.7	15.6	15.6	20.2	20.3	30.1	24.1	27.8
*(GAS, WT% FEED)	12.4	11.9	16.2	20.0	20.2	19.1	21.5	23.1	29.9	23.7	29.3
*(GAS, WT% RECOVERY)	12.6	11.9	16.7	21.0	20.8	20.2	23.1	24.5	32.5	26.5	30.6
to COKE, WT%	3.4	2.6	4.2	3.5	6.6	7.0	7.8	8.2	10.6	7.9	9.8
(WT% C on FEED)	2.8	2.1	3.3	2.7	5.3	5.4	6.0	6.3	8.0	6.0	7.6
(WT% C on RECOVERY)	2.8	2.1	3.4	2.9	5.4	5.	6.4	6.7	8.7	6.7	8.0
UNCONVERTED 600°F+, WT%	62.2	68.8	54.4	45.5	44.6	45.5	32.7	35.0	19.5	27.9	22.7
UNCONVERTED 600°F+, VOL%	63.6	70.3	55.6	46.5	45.6	46.5	33.5	35.8	19.9	28.6	23.2
L PRODUCTS, WT% RECOVERY	100.0	100.0	100.1	100.0	100.0	100.1	100.0	100.0	99.9	99.8	100.1
C <sub>5</sub> - 600°F RECOVERED, VOL%	26.8	22.7	33.4	37.1	38.7	37.4	45.7	42.7	46.5	46.6	46.7

Note: Conversions Determined on a Recovered Weight Basis  
\* Total Gas, Includes C + Components



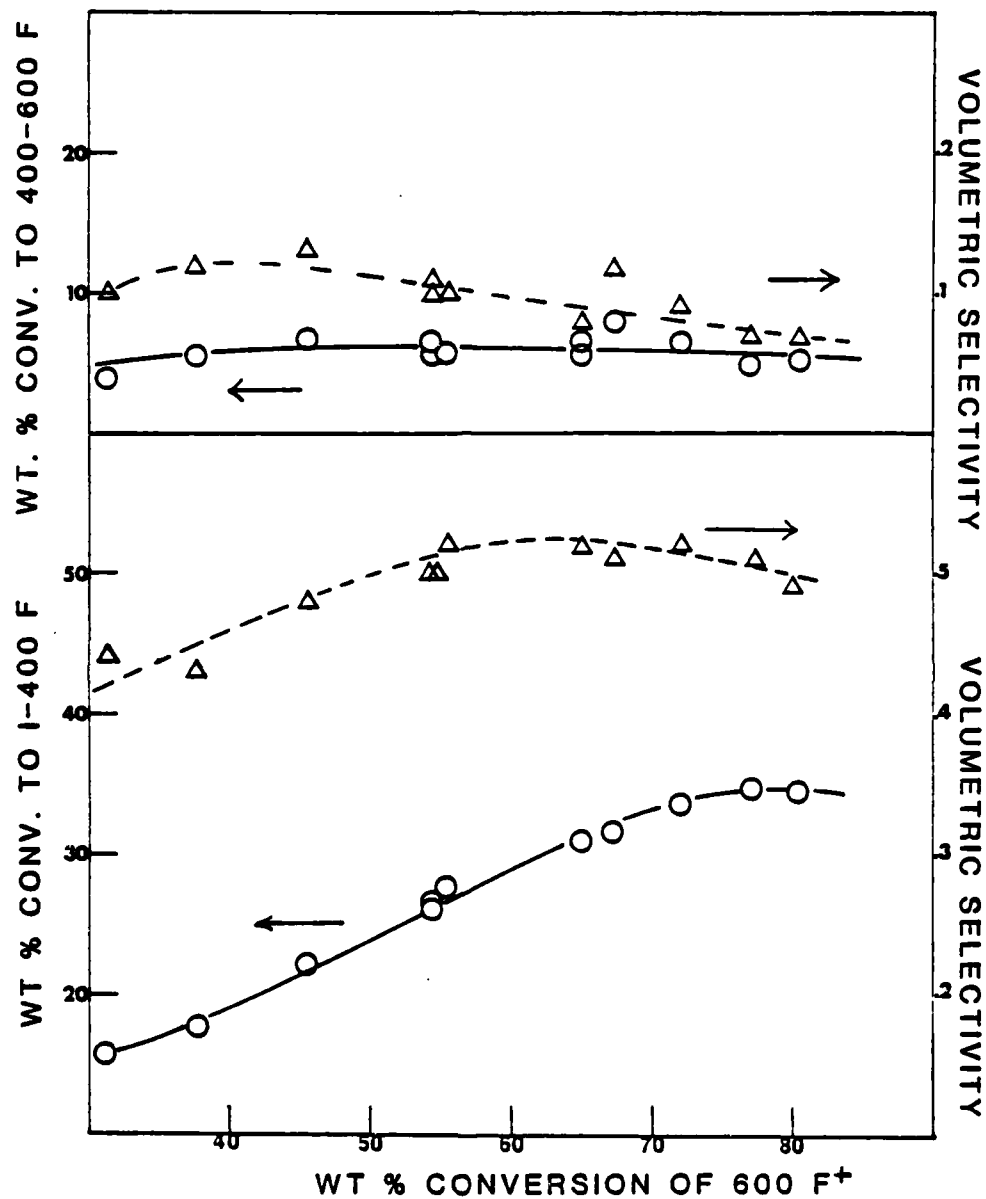


Figure IV-9. Microactivity Test Cracking  
Sample M212 CO-HT

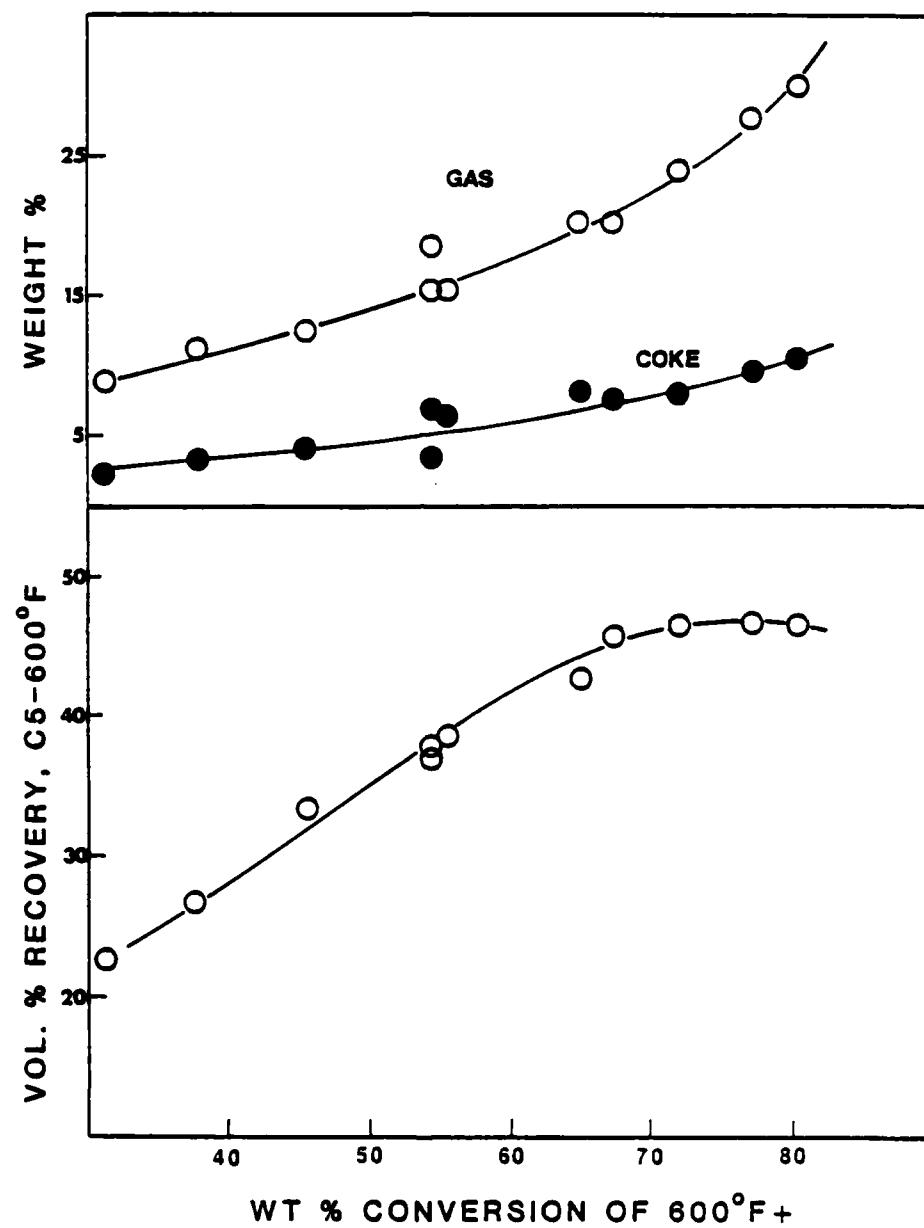


Figure IV-10. Microactivity Test Cracking  
Sample M212 CO-HT

# TABLE IV-14

## PHASE II MAT SUMMARY M221 CO-HT 700°F, PERIOD 8

RUN NO.	139	140	141	142	143	144	145	146	150	151
CATALYST/FEEDSTOCK CONDITIONS	950	950	950	950	1000	1000	1000	1000	1050	1050
TEMP., °F	8.5	5.6	3.3	3.1	3.0	3.3	5.6	5.9	5.6	5.6
CAT./OIL	8.7	8.5	14.4	15.2	15.4	14.1	8.5	8.2	8.6	8.5
WHSV										
TEST RESULTS										
RECOVERY, WT%	96.9	101.3	102.9	101.3	99.5	100.3	93.1	95.5	95.0	95.4
CONVERSION OF 600°F +										
TOTAL CONV., WT%	52.6	54.1	31.8	30.2	45.5	47.4	68.2	69.5	70.4	72.4
to C <sub>5</sub> -400°F, WT%	25.1	27.9	15.7	14.2	19.7	20.4	29.8	29.8	29.8	31.7
VOL. %	30.0	33.4	18.8	16.9	23.6	24.4	35.7	35.7	35.7	38.0
SELECTIVITY	.48	.53	.41	.38	.42	.42	.48	.47	.47	.49
to 400-600°F, WT%	6.9	4.7	2.5	2.0	7.3	6.4	5.7	5.4	3.9	2.7
VOL. %	7.4	5.1	2.7	2.2	7.9	6.9	6.2	5.9	4.3	2.9
SELECTIVITY	.12	.08	.06	.05	.14	.12	.08	.08	.06	.04
to C <sub>6</sub> MINUS GAS, WT%	13.8	15.7	9.8	10.3	14.1	15.7	22.2	22.3	26.1	26.3
*(GAS, WT% FEED)	16.2	20.3	13.7	13.0	16.5	17.9	23.9	24.0	27.5	25.8
*(GAS, WT% RECOVERY)	16.7	20.0	13.3	12.8	16.6	17.9	25.7	25.2	28.9	27.0
to COKE, WT%	6.9	5.7	3.9	3.7	4.4	4.9	10.4	11.8	10.6	11.7
(WT% C on FEED)	5.2	4.5	3.1	2.9	3.4	3.8	7.5	8.8	7.8	8.7
(WT% C on RECOVERY)	5.4	4.4	3.0	2.9	3.4	3.8	8.1	9.2	8.2	9.1
UNCONVERTED 600°F +, WT%	47.4	45.9	68.2	69.8	54.5	52.6	31.8	30.5	29.6	27.6
UNCONVERTED 600°F +, VOL%	48.9	47.4	70.3	72.0	56.2	54.3	32.8	31.5	30.6	28.5
Σ PRODUCTS, WT% RECOVERY	100.1	99.9	100.1	100.0	100.0	100.0	99.9	99.8	100.0	100.0
O <sub>5</sub> - 600°F RECOVERED, VOL%	36.9	38.5	21.5	19.1	31.5	31.3	41.9	41.6	40.0	40.9

Note: Conversions Determined on a Recovered Weight Basis  
\* Total Gas, Includes C<sub>5</sub> + Components

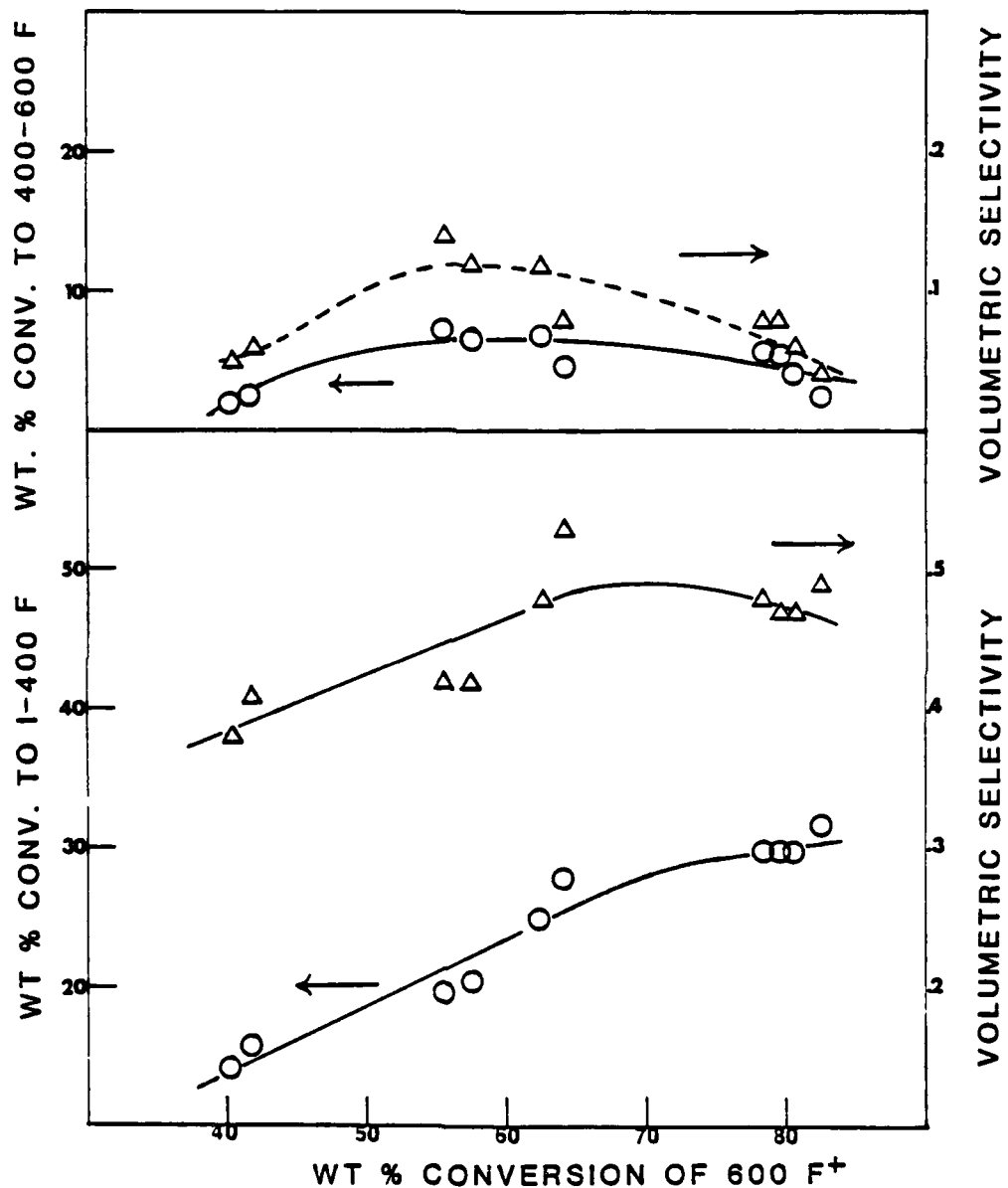


Figure IV-11. Microactivity Test Cracking  
Sample M221 CO-HT

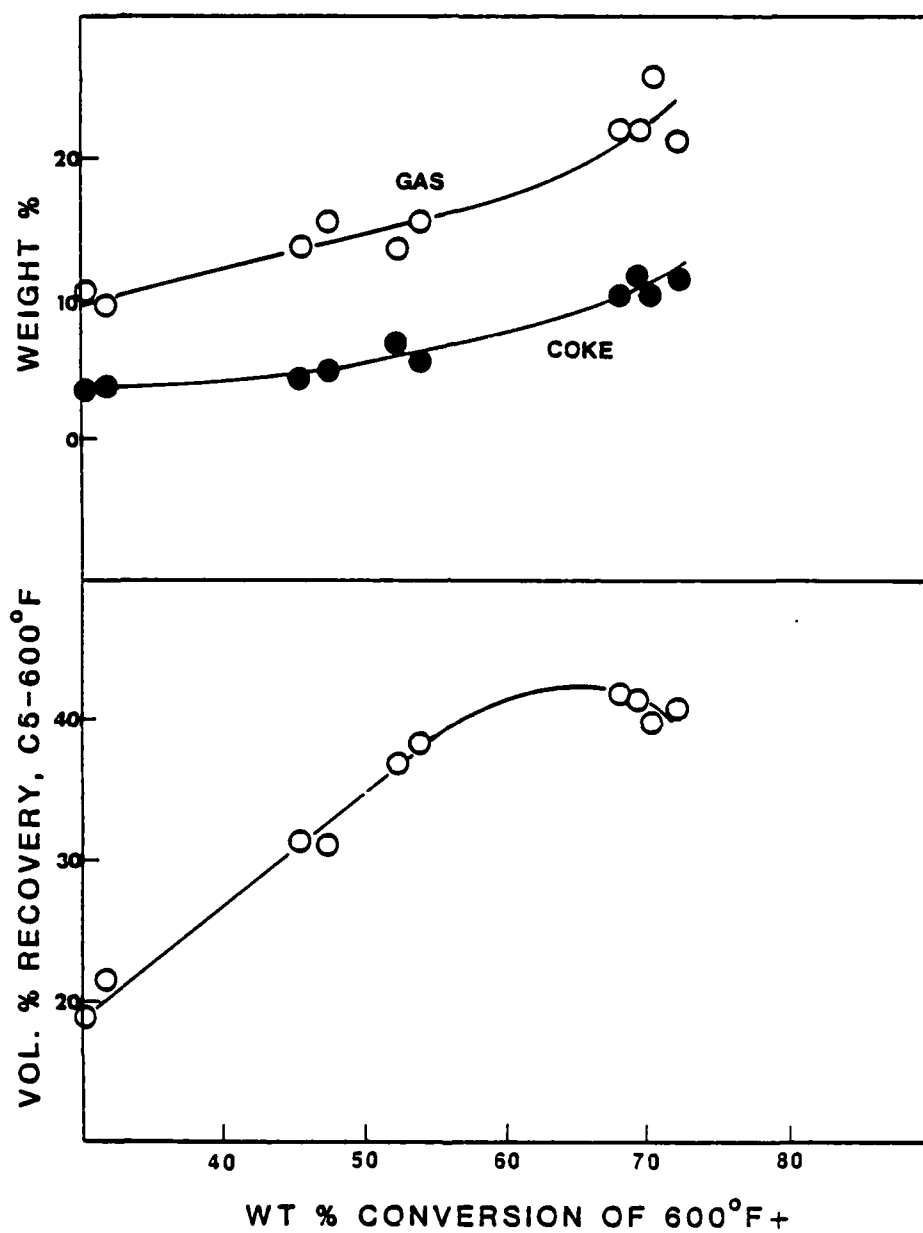


Figure IV-12. Microactivity Test Cracking  
Sample M221 CO-HT

## SECTION V

### EXTRACTION

#### SUMMARY

An important step in the EXTRACTACRACKING process is the extraction of basic nitrogen from shale oil streams. The work was accomplished using mineral acid as the extraction solvent, and was successful in removing greater than 90 percent of the basic nitrogen when performed in a countercurrent extraction column.

A screening study (parameter variation) was set up to determine the effects of acid strength, ratio of hydrocarbon to mineral acid and number of stages. This was done batch-wise with in situ retorted shale oil previously hydrotreated at the Crude Shale Hydrotreater conditions. From this study, reported in Volume II of this report, the recommended conditions for the remainder of the Phase II extraction work were determined.

The M-Series samples were processed on a continuous countercurrent column and good removal of basic nitrogen was accomplished. Also, there were no detrimental effects of the acid such as gum or sludge formation or polymerization of olefins present in the FCC product. The hydrocarbon product raffinates were washed with water.

The GC-2 group of large volume samples (called PHO-1, 2, 3, and 4) were then processed for the above-ground retorted shale source. The four GC-2 samples were subjected

to the same continuous extraction technique as were the M-Series samples. The GC-2 hydrocarbon raffinates were then washed followed by a water wash which effectively removed traces of mineral acid contaminants. Acid contaminants have adverse effects on catalyst activity of the succeeding processing step.

#### OBJECTIVE

The purpose of nitrogen extraction is to remove a large portion of the basic nitrogen from the naphtha and mid-distillate range straight run and fluid catalyst cracked shale oil without the use of hydrogen.

#### MECHANICAL DESCRIPTION

The conditions for optimal removal of basic nitrogen compounds were determined by a screening study and reported in Volume II of this report. A continuous countercurrent extraction column was set up for the remainder of the Phase II sample preparations. Residence time and ratio of hydrocarbon to acid were controlled by constant volume bellows feed pumps. Acid strength was controlled by premixing the acid solution feedstock. The column interface level was controlled by the addition of an external standpipe.

After extraction, the raffinate (hydrocarbon phase product) was washed in batch glassware. The M-Series samples were water washed and the GC-2 samples were washed in an additional cleanup step followed with deionized water.

## CHEMICAL DESCRIPTION

The extraction of nitrogen compounds from the shale oil is effected by an aqueous solution of mineral acid. The concentration of the solution was determined in the screening study to be about 40 to 50 percent for optimum extraction. This is described in the experimental procedure following.

In order to remove residual acid from the hydrocarbon raffinate after extraction, a dilute aqueous solution of sodium hydroxide was used. This was followed by water washing to remove residual sodium.

No catalyst was required.

## EXPERIMENTAL PROCEDURE

### 1. CONTINUOUS EXTRACTION OF M-SERIES SAMPLES

The continuous countercurrent extraction column was set up using constant volume bellows feed pumps and an external siphon breaker interface level control. Acid (at the strength and dosage found from the screening study to be an efficient extraction medium) was pumped to the top feed port of the column while the shale oil to be contacted was pumped into the lower feed port. The feed material was a material balance blend of IBP-cutpoint from the Crude Shale Hydro-treater and the Fluid Cracking Reactor. Cutpoint was defined as 500°F or 600°F depending upon the final product desired. For two of the samples the SR (straight run) material and CR (cracked) material were not blended, but



contacted separately to determine the effect of the extraction medium on the bromine number of the shale oil. A reduction in the bromine number, if encountered, would indicate acid catalyzed polymerization of the olefins in the cracked portion of the feedstock.

The column temperature was controlled at a temperature which would aid phase separation but not evaporate or boil off any hydrocarbon. This was controlled by a heat tape wrapped around the column and fitted with a Variac® voltage controller and several thermocouples and temperature readouts. After extraction was completed the product raffinate was water washed to remove residual mineral acid. Recoveries of hydrocarbon averaged 88.4 weight percent.

## 2. CONTINUOUS EXTRACTION OF ABOVE-GROUND GC-2 SHALE OIL

Fuel samples were prepared from above-ground retorted shale oil by subjecting the full range Crude Shale Hydro-treater products to the FCC, followed by nitrogen extraction of the IBP to 600°F fraction. The extractions were performed in the countercurrent extraction column in much the same manner as the M-Series samples. The washing steps were incorporated to remove traces of mineral acid and sodium which might deactivate catalysts in further processing steps. Washing steps were done in the countercurrent extraction column at a 1:1 hydrocarbon to aqueous phase. The temperature was controlled at about 110°F to aid in phase separation.

## EXPERIMENTAL RESULTS

A. Continuous extraction for the M-Series samples was set up according to the same conditions developed in the preliminary screening study which is reported in Volume II of this report. Since samples were available separately of straight run and cracked IBP to cutpoint, these were blended for all but two runs in which they were processed separately. Any change in the high bromine numbers of the cracked feedstock during extraction would give an indication of olefin polymerization by, or removal in, the acidic aqueous phase. Results of these extractions are shown in Table V-1. Products were water washed before further processing.

B. The GC-2 above-ground retorted shale oil samples (after initial hydrotreatment, FCC, and appropriate distillation and blending) were processed in four separate extractions at conditions determined as optimum for basic nitrogen removal. The continuous extraction column was set up to make use of as many as seven actual stages for mixing, two for separation of phases. Results are shown in Table V-2. Products were washed twice to remove any carryover impurities. These steps effectively removed the residual mineral acid to <1 ppm and all contaminants to <5 ppm in products which were further processed (Section VII).

TABLE V-1

# M-SERIES CONTINUOUS EXTRACTION RESULTS FOR ABOVE-GROUND SHALE OIL DISTILLATES

	M-211				M212				M-221			
	SR+CR		SR+CR		SR		SR		SR		SR	
	FEED	RAFF	FEED	RAFF	FEED	RAFF	FEED	RAFF	FEED	RAFF	FEED	RAFF
API	41.6	43.8	35.6	39.4	40.7	42.4	37.0	40.6	42.0	44.0		
BR. NO.	51.2	49.4	29.2	27.7	100.8	88.5	27.0	24.8	103.5	99.0		
S, WT%	0.15	0.19	0.17	0.18	0.21	0.21	0.15	0.18	0.16	0.15		
N. (BASIC) WT%	1.117	0.226	1.136	0.312	0.779	0.042	1.070	0.178	0.741	0.031		
N REMOVAL %	-	79.7	-	72.6	-	94.6	-	83.3	-	95.8		
HC REMOVAL %	-	6.1	-	-	-	14.4	-	-	-	13.6		
SIM D, WT%												
IBP	145		306		122		246		134			
2	208		329		164		287		155			
10	296		381		221		352		208			
50	414		508		389		488		362			
90	488		602		543		580		531			
98	511		625		613		597		605			
EP	552		631		657		753		658			

**TABLE V-2**  
**CONTINUOUS EXTRACTION RESULTS FOR**  
**THE GC-2 ABOVE-GROUND SHALE OIL DISTILLATES**

	PHO-1		PHO-2		PHO-3		PHO-4	
	<u>Feed</u>	<u>Raff</u>	<u>Feed</u>	<u>Raff</u>	<u>Feed</u>	<u>Raff</u>	<u>Feed</u>	<u>Raff</u>
API	36.9	39.3	38.5	39.8	36.7	39.5	41.7	41.3
BR NO.	62	51	52	51	53	60	54	46
S, WT. %	0.14	0.13	0.14	0.13	0.18	0.18	0.21	0.20
N (B) WT. %	0.646	0.021	0.585	0.005	0.795	0.023	0.802	0.089
N REMOVAL %	-	96.8	-	99.1	-	97.1	-	88.9
HC REMOVAL %	-	8.6	-	11.0	-	8.3	-	8.9
SIM D, WT%								
IBP	184	-	177	156	171	143	123	-
2	219	-	220	207	201	178	161	-
10	292	-	291	286	325	281	237	-
50	439	-	426	435	467	448	423	-
90	555	-	525	543	578	559	545	-
98	610	-	575	573	595	577	579	-
EP	685	-	605	585	660	587	649	-

Continuous countercurrent extractions confirmed both the nitrogen removal and the required acid strength. An acid strength of 41.9 weight percent was used and resulted in predictable results both in total hydrocarbon removed and in percent basic nitrogen removed.

The dosage of acid to hydrocarbon required was determined by a set of three stage extractions, using four acid strengths. Figure V-1 shows that at 41.9 percent acid strength, a 10 percent dosage removes 90 to 95 percent of the basic nitrogen.

The data from the screening study were used to establish the operating conditions for the continuous runs.

#### M-SERIES EXTRACTIONS

The first series of continuous extractions were conducted on samples in the process scheme. Straight run naphtha (IBP to cutpoint) and FCC naphtha were combined and extracted at conditions determined in the screening study. The continuous extraction utilized up to six actual stages of the countercurrent extraction column and, as a result, showed excellent efficiency in nitrogen removal. Table V-3 shows the operating data for the runs and points out that the conditions were held very close to those indicated from the screening runs.

The feeds for two sets were not combined but treated separately as SR and FCC naphtha in order to determine the effect of contact with mineral acid on the FCC naphtha. Bromine numbers which give an indication of olefin content

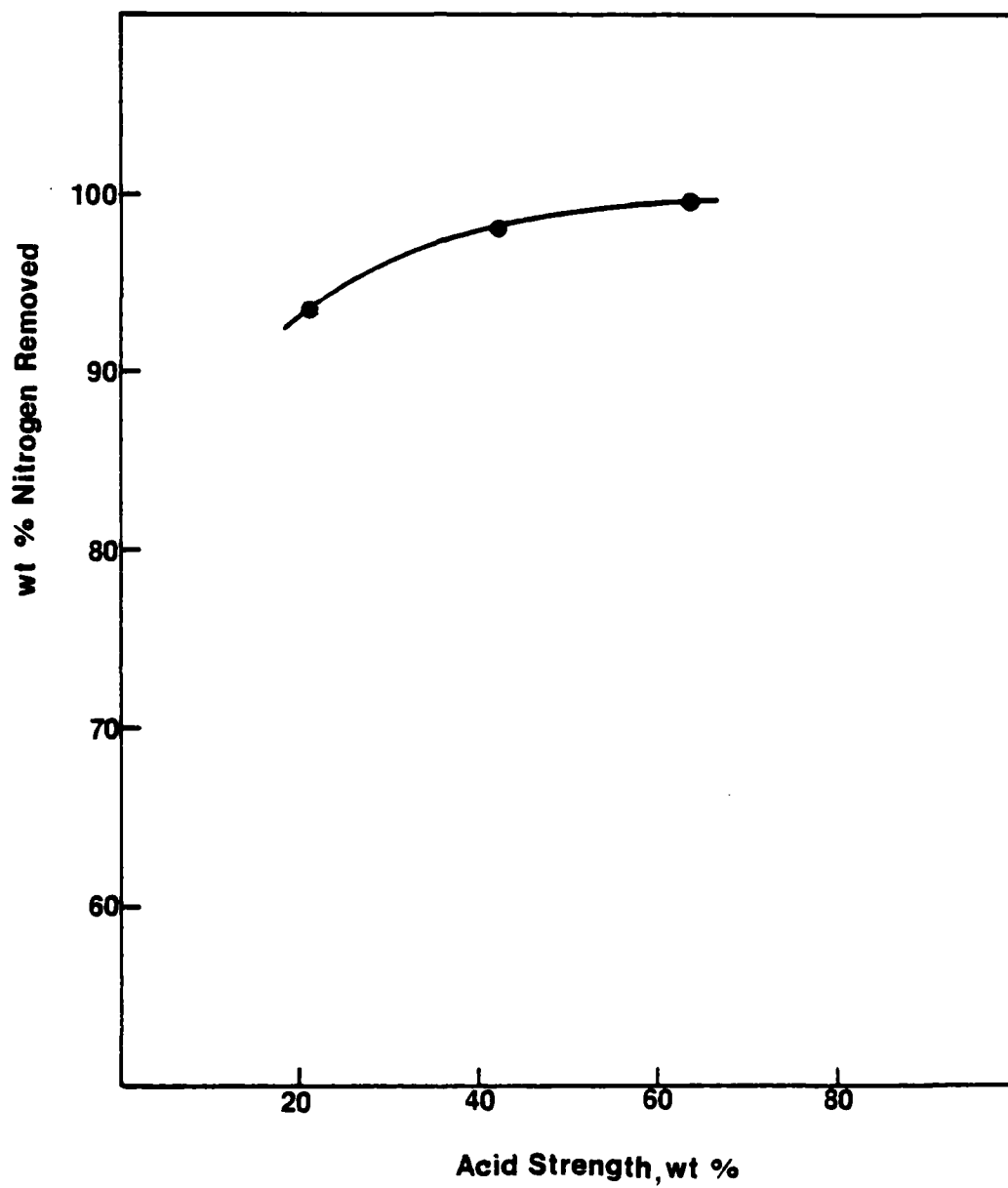


Figure V-1. Nitrogen Removal In Three Equilibrium Stages At 10 Wt. % Dosage

TABLE V-3

OPERATING DATA TABLE FOR CONTINUOUS  
EXTRACTIONS OF ALL ABOVE-GROUND  
SHALE OIL DISTILLATES.

	RUN	PHO 1	PHO 2	PHO 3	PHO 4	M 211	M 212 SR	M 212 CR	M 221 SR	M 221 CR
HC FEED	<u>1.</u>	100	100	100	100	100	100	100	100	100
ACID FEED	<u>1.</u>	25.6	14.7	16.0	18.0	21.5	15.9	16.3	16.0	16.2
HC RECOVERY	<u>1.</u>	90.8	89.0	91.7	91.1	93.9	85.3	86.8	85.7	88.3
AQUEOUS RECOVERY	<u>1.</u>	34.8	25.7	24.2	26.9	27.6	34.6	29.4	33.3	28.0
MAT'L BAL CLOSURE		100.0	100.0	99.9	100.0	100.0	103.5	99.9	102.6	100.1
COLUMN TEMP °F		86	85	87	86	86	86	86	86	86
CONTACT TIME	<u>2.</u>	21	21	21	21	21	21	21	21	21
ACID STRENGTH	<u>3.</u>	41.9	41.9	41.9	41.9	41.9	41.9	41.9	41.9	41.9
HC: ACID RATIO (WT.)		3.9	6.8	6.2	5.6	4.7	6.3	8.6	6.2	6.2

1. BASED ON WT% OF HC FEED

2. IN MINUTES

3. WT% ACID IN AQUEOUS SOLUTION

were examined before and after extraction and it was evident that no undue polymerization or gum formation occurred. Table V-1 gives the analytical results for the runs showing basic nitrogen removal, Bromine numbers and hydrocarbon recoveries. It should be pointed out that the nitrogen-containing hydrocarbon removed with the aqueous phase is recoverable for further use.

After subjection to extraction, the raffinates were washed with water and processed further in the EXTRACTA-CRACKING scheme.

#### ABOVE-GROUND RETORTED SHALE OIL

Four samples of above-ground retorted GC-2 shale oil were produced separately on the continuous extraction column. The operating conditions are shown in Table V-3. The temperatures were controlled at 86°F and no problem occurred with phase separation. Acid feed rates were adjusted for a volumetric ratio of 10:1 hydrocarbon to acid phase. Actual weight ratios are also reported in the operating data. Contact time was approximately 21 minutes.

Removal of basic nitrogen was about 96 percent (average) as shown in Table V-2. Hydrocarbon removal was less than 10 percent. No significant changes occurred in bromine numbers, indicating no effect upon olefin content.

Product from these runs were subjected to dual washing to prevent residual acid from deactivating the catalyst during guardcase hydrotreating.



## CONCLUSIONS

From the screening study (as reported in Volume II) it was determined that significant basic nitrogen could be extracted from the previously hydrotreated shale oil. Conditions were established for future continuous processing as follows:

Acid Dosage	1:10	(Acid to HC volume ratio)
Acid Strength	40-60%	
Number Stages	>2	

The M-Series samples were successfully extracted on the continuous column utilizing only four contact stages. Predictable basic nitrogen removal of up to 95.8 percent was accomplished.

The above-ground GC-2 samples were also extracted with up to 99 percent removal of basic nitrogen. These samples were caustic washed and water washed for removal of trace amounts of mineral acid.

In the cases involving cracked naphtha, no problems were encountered due to potential polymerization or gum formation.

Operations at temperatures around 100°F suggest better phase separation and no "cuff" layer formation.

Conditions recommended for Phase III Pilot Plant Preparation of Samples are as outlined in Table V-4.

TABLE V-4

OPERATING PARAMETERS  
FOR EXTRACTION

	<u>PHASE II</u>	<u>PHASE III (RECOM)</u>
<u>ACID EXTRACTION</u>		
Column Diameter, in. I. D.	1.0	2.0
Hydrocarbon Feed Rate, ml/min	22.0	115.0
Acid Feed Rate, ml/min	2.2	15.0
Acid Strength wt. % $H_3PO_4$	41.9	41.9
Residence Time, min.	21	13
Column Temperature, °F	75 - 150	110 - 115
<u>H<sub>2</sub>O Washing</u>		
Hydrocarbon Feed Rate, ml/min	—*	300
H <sub>2</sub> O Feed Rate, ml/min.	—	300
Column Temperature, °F	—	110

\*Batchwise

SECTION VI  
RECYCLE OIL HYDROTREATER

SUMMARY

The operation of the cycle oil hydrotreater for a total of nine nominal twelve-hour material balance periods indicates that the M-Series above-ground shale oil streams could effectively be hydrotreated. At the 650/700/750°F run temperatures and 1000/1400 psig run pressures, desulfurization ranged from 61 to 94 percent, while denitrogenation ranged from 22 to 79 percent. The product streams appear to easily meet all military fuel oil specifications, except the pour point (due to the high level of paraffins).

OBJECTIVES

The major objective of the series of cycle oil hydrotreating runs on the above-ground shale oil was to determine the optimum operating conditions necessary to hydrotreat FCC bottoms produced via the EXTRACTACRACKING process to a relatively low nitrogen, low sulfur level fuel oil. The study would also show that the FCC bottoms stream could easily be upgraded through hydrotreating to provide streams for FCC recycle or for further processing to make heavy fuel oil.

FEEDSTOCKS

Three above-ground shale oil samples coded M-211, M-212 and M-221 were used as feedstock for the series of

cycle oil hydrotreating runs. In carrying out the experimental scheme of the EXTRACTACRACKING process each had been hydrotreated in the crude shale hydrotreater (CSHT), fractionated into a heavy (high boiling) cut, cracked in an FCC unit and finally once more fractionated into a heavy cut. The simple schematic diagrams of Figure VI-1 show the processing of all three feedstocks before the cycle oil hydrotreater.

The available properties of the three respective feedstocks are given in Tables VI-1 through VI-3. Before the feedstocks were hydrotreated they were filtered in an effort to remove FCC catalyst fines due to the high carryover rates routinely observed in small laboratory FCC units.

#### EQUIPMENT

In the M-Series above-ground shale cycle oil hydrotreating studies, a nominal one-inch trickle flow laboratory reactor was used analogous to that used in the crude shale oil hydrotreating of Sample M-221. Figure VI-2 gives a schematic diagram of the actual equipment set-up, showing that the main differences between the cycle oil set-up and that for the other hydrotreating runs were: (1) the absence of a guardbed for catalyst protection, (2) a different method of regulating reactor pressure, (3) the absence of a mist separator in the gas stream after liquid collection, and (4) the use of three PID controllers driven by external skin temperature thermocouples instead of four, to provide temperature control for the reactor. Once

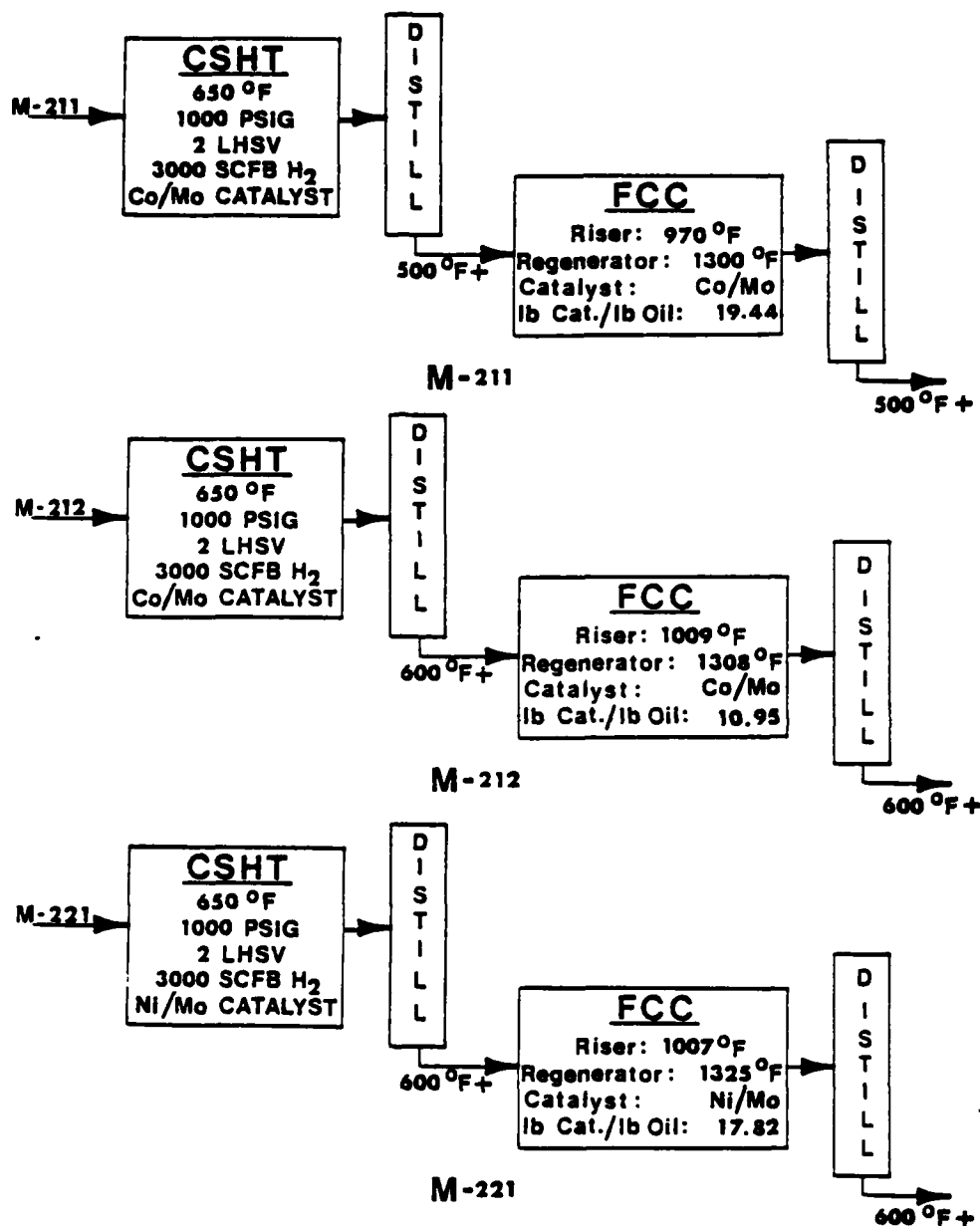


Figure VI-1. Processing Of M-Series Above-ground Shale Before Cycle Oil Hydrotreating

**TABLE VI-1**

**FEED CHARACTERIZATION - CYCLE OIL  
HYDROTREATING SAMPLE M211**

<b>Properties:</b>		<b>Distillation, °F:</b>	
°API	23.0	<b>Wt % By</b>	
Carbon, Wt %	-	<b>IBP</b>	439
Hydrogen, Wt %	-	<b>2</b>	475
Nitrogen, Wt %	1.65	<b>10</b>	587
Basic Nitrogen, Wt %	-	<b>30</b>	612
Sulfur, Wt %	0.18	<b>50</b>	688
Oxygen, Wt %	-	<b>70</b>	775
Ramsbottom Carbon, Wt %	1.20	<b>90</b>	885
Aromatics, Wt %	-	<b>98</b>	968
		<b>EP</b>	1003

TABLE VI-2

FEED CHARACTERIZATION - CYCLE OIL  
HYDROTREATING SAMPLE M212

Properties:		Distillation, °F:	
°API	18.4	Wt % By	
Carbon, Wt %	-	IBP	492
Hydrogen, Wt %	-	2	546
Nitrogen, Wt %	2.05	10	634
Basic Nitrogen, Wt %	-	30	698
Sulfur, Wt %	0.22	50	762
Oxygen, Wt %	0.231	70	833
Ramsbottom Carbon, Wt %	1.83	90	921
Aromatics, Wt %	-	98	980
		EP	995

**TABLE VI-3**

**FEED CHARACTERIZATION - CYCLE OIL  
HYDROTREATING SAMPLE M221**

<b>Properties:</b>		<b>Distillation, °F:</b>	
°API	19.6	Wt % By	
Carbon, Wt %	-	IBP	491
Hydrogen, Wt %	-	2	531
Nitrogen, Wt %	1.83	10	601
Basic Nitrogen, Wt %	-	30	662
Sulfur, Wt %	0.17	50	723
Oxygen, Wt %	0.197	70	797
Ramsbottom Carbon, Wt %	2.04	90	892
Aromatics, Wt %	-	98	967
		EP	999



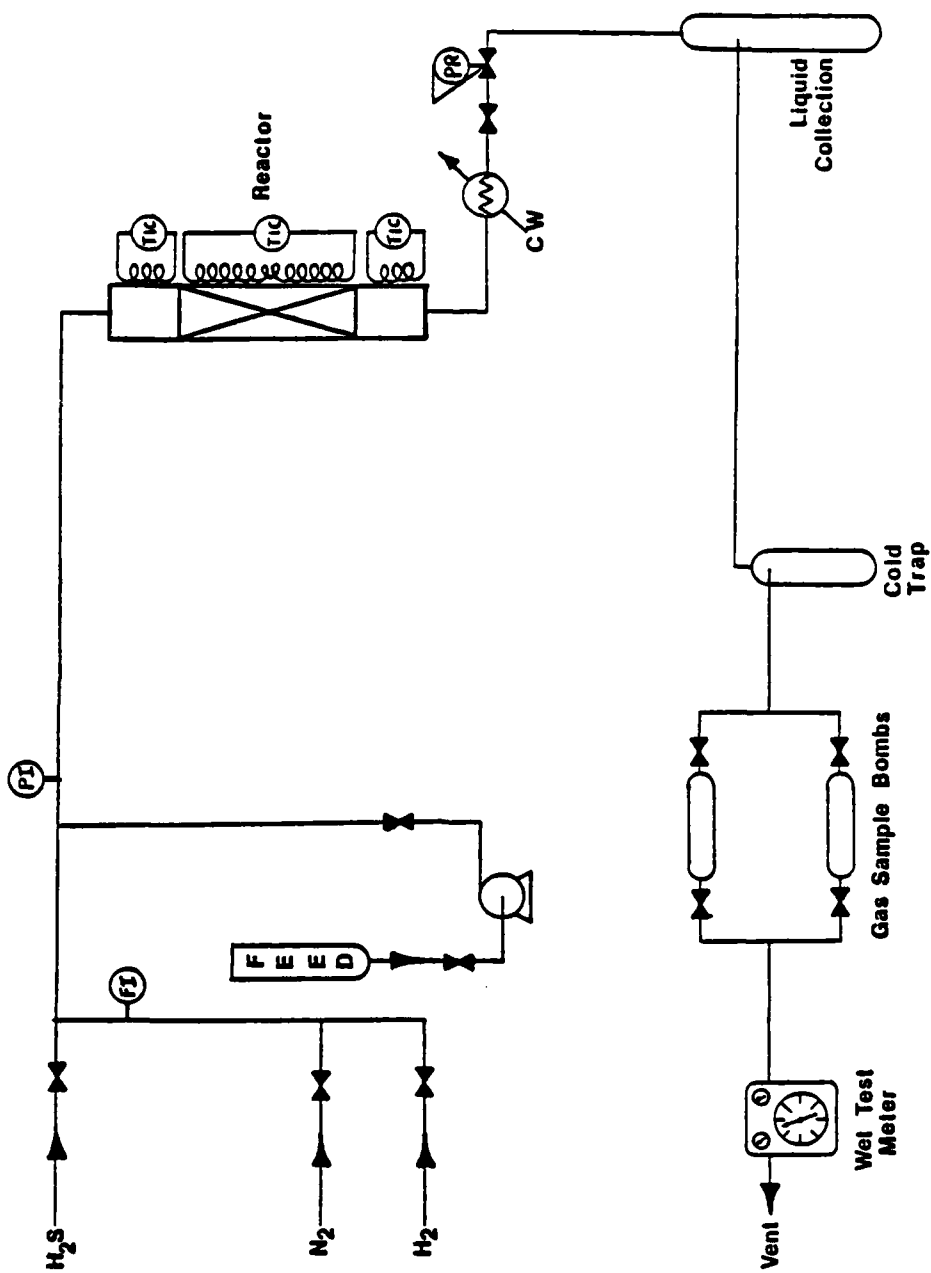


Figure VI-2. Schematic Diagram Of Cycle Oil Hydrotreating Set-up

again, for these runs heating lamps and heating tapes were used to keep the feed flowing more easily and avoid pump problems. Although the nitrogen and hydrogen lines to the reactor were also different, the same overall function was provided by the set-up.

#### EXPERIMENTAL PROCEDURE

Table VI-4 shows the desired nominal operating conditions and test period scheduling for the cycle oil hydro-treating studies on the above-ground shale oil feeds. The last material balance at 750°F continued until the feed was exhausted.

The reactor for each feedstock was packed first with inert tabular alumina. The catalyst bed, consisting of 50 cc of a nickel molybdate catalyst and 50 cc of Ottawa sand, was then centered in the reactor with the sand and catalyst added alternately in 10 cc increments. The remaining section of the reactor was packed with inert tabular alumina.

Before each feedstock was fed to the reactor, the reactor was pressure checked first with nitrogen, then with hydrogen to roughly 100 psig over the nominal operating pressure. Presulfiding the catalyst was accomplished with H<sub>2</sub>S at bottle pressure and 50°F over the maximum desired run temperature or at 800°F. The reactor was then allowed to cool, the hydrogen flow rate set to 0.944 SCFH or 3000 SCFB, and the reactor repressurized to the appropriate run pressure. After initiating feed to the reactor, the bed

TABLE VI-4

OPERATING CONDITIONS OF  
CYCLE OIL HYDROTREATER

SAMPLE ID	M-211-CO	M-212-CO	M-221-CO
°API	23.0	18.5	19.7
SHALE OIL TYPE	ABOVE- GROUND	ABOVE- GROUND	ABOVE- GROUND

CONSTANT OPERATING CONDITIONS:

PRESSURE, PSIG	1000	1400	1000
LHSV, hr <sup>-1</sup>	1	1	1
H <sub>2</sub> RATE, SCFB	3000	3000	3000
CATALYST	NI/MO	NI/MO	NI/MO
CATALYST CHARGE, cc	50	50	50

PERIOD (HRS) TEMPERATURE, °F

12	LINEOUT, 650°F
24	MATERIAL BALANCE, 650°F
36	LINEOUT, 700°F
48	MATERIAL BALANCE, 700°F
60	LINEOUT, 750°F
END OF FEED	MATERIAL BALANCE, 750°F

temperature was slowly brought up to 650°F or the first run temperature for each feed. Conditions were monitored continuously and recorded hourly to maintain them at the levels delineated above. Twelve hour lineout periods were allocated between the tests as indicated in Table VI-4. Each test period consisted of a twelve-hour material balance to end-of-feed for the 750°F tests.

The product samples taken from the reactor were stabilized; that is, stripped of water, ammonia, and hydrogen sulfide on an Oldershaw fractionation column. This stripping was performed at atmospheric pressure and a temperature greater than 300°F for two to three hours, after which samples were submitted for various analyses to characterize the products.

## RESULTS

The operating results for the cycle oil hydrotreating studies on the above-ground shale oil feeds are presented in Table VI-5 and VI-6. These results include operating conditions averaged over the given test length, along with material balances based on weight percent of feed.

On the same tables are listed the available product properties for the stabilized or stripped full range hydro-treated product, except all product samples from the M-221 series were cut into two different boiling range fractions as shown in Tables VI-7 through VI-10. The available analyses for these product cuts are given in the same tables. The results for each feedstock led to the plots of percent

TABLE VI-5

# CYCLE OIL HYDROTREATING ABOVE-GROUND SHALE OIL

Feed	M-	211	211	211	212	212
Period / <small>TEST LENGTH, Hr</small>		1/12	2/12	3/11	4/12	5/12
OPERATING CONDITIONS						
Temperature, °F		650	700	750	650	700
Pressure, PSIG		1000	1000	1000	1400	1400
LHSV, Hr <sup>-1</sup>		1	1	1	1	1
H <sub>2</sub> Rate, SCFB		3032	3000	3071	2976	3098
MATERIAL BALANCE						
Weight Percent of Feed						
Feed		100	100	100	100	100
H <sub>2</sub> In		4.9	5.0	5.1	4.8	5.0
Subtotal In		104.9	105.0	105.1	104.8	105.0
H <sub>2</sub> O		(0.26)	(0.26)	-	(0.26)	(0.26)
NH <sub>3</sub>		(0.43)	(0.96)	-	(0.90)	(1.47)
H <sub>2</sub> S		(0.14)	(0.17)	-	(0.13)	(0.21)
H <sub>2</sub> Out		4.5	4.2		4.3	4.1
C <sub>1</sub>		-	0.16	No	0.20	0.20
C <sub>2</sub>		0.32	0.19	GAS	-	0.10
C <sub>3</sub>		0.32	0.17	Analysis	0.35	0.10
C <sub>4</sub>		0.22	0.13	Performed	0.34	0.12
C <sub>5</sub>		0.19	0.14		0.08	0.07
Stabilized Liquid		101.8	98.92	97.5	97.5	96.8
Subtotal		108.18	105.30	-	104.11	103.43
Closure		103.1	100.3	-	99.3	98.5
Hydrogen Consumption, SCFB		248	484	-	311	560
PRODUCT PROPERTIES						
°API		26.0	27.3	29.1	22.7	24.8
Sulfur, Wt %		0.043	0.024	*	0.053	0.024
Nitrogen, Wt %		1.27	0.87	*	1.34	0.37
Oxygen, Wt %		-	-	-	-	-
Viscosity 100°F, cSt		15.4	12.6	*	36.6	26.8
" 210°F, cSt		3.08	2.76	*	4.96	4.26
Pour Point, °F		65	60	*	65	65

\* No Analysis performed

TABLE VI-6

**CYCLE OIL HYDROTREATING  
ABOVE-GROUND SHALE OIL**

Feed	M-	212	221	221	221
Period	TEST LENGTH, Hr	6/12	7/12	8/12	9/8
<b>OPERATING CONDITIONS</b>					
Temperature, °F		750	650	700	750
Pressure, PSIG		1400	1000	1000	1000
LHSV, Hr <sup>-1</sup>		1	1	1	1
H <sub>2</sub> Rate, SCFB		3129	2904	3024	2920
<b>MATERIAL BALANCE</b>					
Weight Percent of Feed					
Feed		100	100	100	100
H <sub>2</sub> In		5.0	4.7	4.9	4.7
Subtotal In		105.0	104.7	104.9	104.7
H <sub>2</sub> O		(0.26)	(0.22)	(0.22)	(0.22)
NH <sub>3</sub>		(1.97)	(0.50)	(0.94)	(1.33)
H <sub>2</sub> S		(0.22)	(0.11)	(0.15)	(0.15)
H <sub>2</sub> Out		3.6	4.2	3.9	3.7
C <sub>1</sub>		0.7	-	0.09	0.34
C <sub>2</sub>		0.9	0.06	0.74	0.96
C <sub>3</sub>		1.0	0.12	0.69	1.04
C <sub>4</sub>		0.8	0.07	0.40	0.73
C <sub>5</sub>		0.7	0.26	0.24	0.46
Stabilized Liquid		95.6	99.88	99.39	111.94
Subtotal		105.75	105.42	107.26	120.92
Closure		100.7	100.7	102.2	115.5
Hydrogen Consumption, SCFB		973	309	617	618
<b>PRODUCT PROPERTIES</b>					
°API		27.0	22.8	23.8	25.7
Sulfur, Wt %		0.014	*	*	*
Nitrogen, Wt %		0.45	*	*	*
Oxygen, Wt %		-	-	-	-
Viscosity 100°F, cSt		14.77	*	*	*
" 210°F, cSt		3.17	*	*	*
Pour Point, °F		65	*	*	*

\* No analyses performed on full range product. Analyses for fractions are given in Tables VII 9 through VII 10.

TABLE VI-7

DISTILLATION OF FULL RANGE  
CYCLE OIL HYDROTREATED  
ABOVE-GROUND SHALE OIL M211

OPERATING CONDITIONS			
Temperature, °F	650	700	750
Pressure, PSIG	1000	1000	1000
LHSV, Hr <sup>-1</sup>	1	1	1
H <sub>2</sub> Rate, SCFB	3032	3000	3071

Distillation, °F:			
Wt % By			
IBP	440	351	-
2	466	416	-
10	535	511	-
30	606	590	-
50	684	666	-
70	776	756	-
90	889	864	-
98	980	937	-
EP	*	957	-

\* Beyond temperature limit of distillation device.

TABLE VI-8

**DISTILLATION OF FULL RANGE  
CYCLE OIL HYDROTREATED  
ABOVE-GROUND SHALE OIL M-212**

OPERATING CONDITIONS			
Temperature, °F	650	700	750
Pressure, PSIG	1400	1400	1400
LHSV, Hr <sup>-1</sup>	1	1	1
H <sub>2</sub> Rate, SCFB	2976	3098	3129

Distillation, °F:			
Wt % By			
IBP	414	396	235
2	497	469	332
10	601	587	507
30	681	674	645
50	748	741	709
70	819	820	786
90	906	918	878
98	965	1006	942
EP	981	*	958

\* Beyond temperature limit of distillation device.



**TABLE VI-9**

**CYCLE OIL HYDROTREATING  
ABOVE-GROUND SHALE OIL M221  
PRODUCT PROPERTIES 600°F+ CUT**

OPERATING CONDITIONS			
Temperature, °F	650	700	750
Pressure, PSIG	1000	1000	1000
LHSV, Hr <sup>-1</sup>	1	1	1
H <sub>2</sub> Rate, SCFB	2904	3024	2920
PRODUCT PROPERTIES			
°API	21.7	23.0	24.1
Carbon, Wt %	-	-	-
Hydrogen, Wt %	-	-	-
Nitrogen, Wt %	1.40	1.09	0.63
Basic Nitrogen, Wt %	0.680	0.509	0.331
Sulfur, ppm Wt%	0.070	0.036	0.027
Distillate Yield, Wt%	90.3	85.89	82.05
Ramsbottom Carbon, Wt %	0.90	0.90	0.78
Viscosity 100°F, cSt	41.59	37.08	27.89
" 210°F, cSt	5.13	4.95	4.35
Pour Point, °F	65	65	65
Distillation, °F:			
Wt % By			
IBP	541	580	552
2	583	594	576
10	620	626	616
30	679	684	672
50	743	745	727
70	820	818	795
90	929	917	881
98	*	1002	943
EP	*	*	959

\* Beyond temperature limit of Sim D device.

TABLE VI-10

**CYCLE OIL HYDROTREATING  
ABOVE-GROUND SHALE OIL M221  
PRODUCT PROPERTIES IBP-600°F CUT**

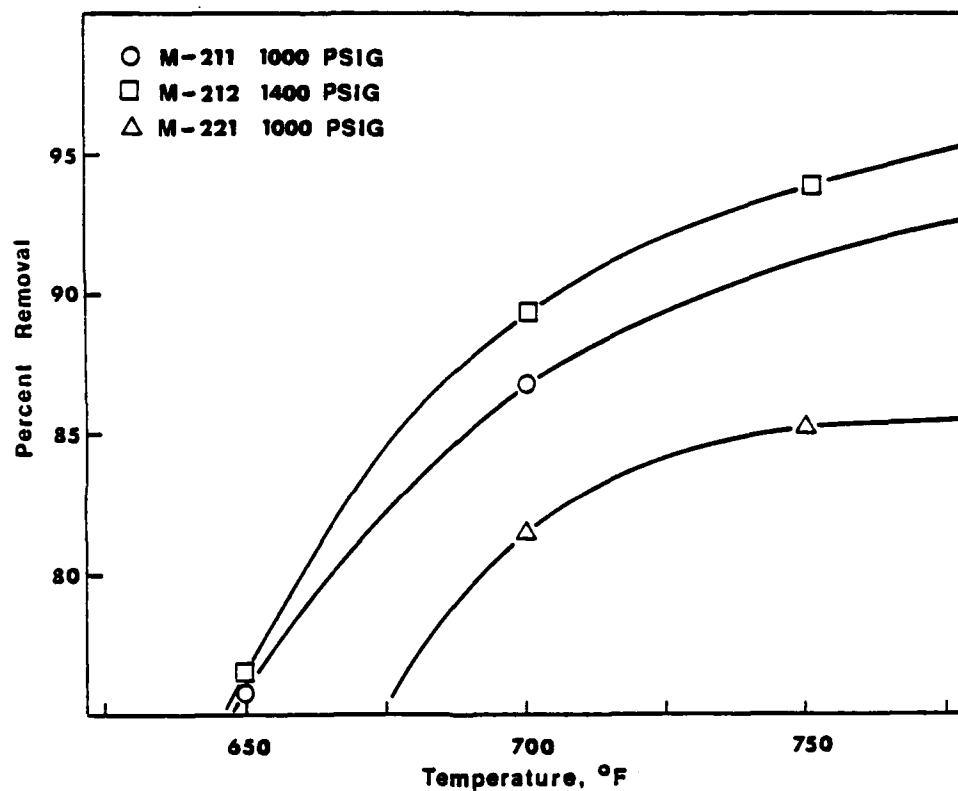
OPERATING CONDITIONS			
Temperature, °F	650	700	750
Pressure, PSIG	1000	1000	1000
LHSV, Hr <sup>-1</sup>	1	1	1
H <sub>2</sub> Rate, SCFB	2904	3024	2920
PRODUCT PROPERTIES			
°API	28.0	21.2	38.0
Carbon, Wt %	(86.70)	(86.88)	(86.87)
Hydrogen, Wt %	11.69	12.28	12.57
Nitrogen, Wt %	1.57	0.94	0.56
Basic Nitrogen, Wt %	0.985	0.603	0.315
Sulfur, ppm WT %	0.0367	0.0042	0.0034
Distillate Yield, WT %	9.70	14.11	17.95
Ramsbottom Carbon, Wt %	-	-	-
Viscosity 100°F, cSt	-	-	-
" 210°F, cSt	-	-	-
Pour Point, °F	-	-	-
Distillation, °F:			
Wt % By D2887-73			
IBP	304	336	158
2	353	365	203
10	455	444	322
30	517	511	445
50	549	547	504
70	581	581	546
90	615	618	599
98	658	646	649
EP	724	658	720

desulfurization and percent denitrogenation versus reaction temperature shown in Figures VI-3 and VI-4. Simulated distillations for the product samples other than the M-221 product samples are given separately in Tables VI-7 and VI-8.

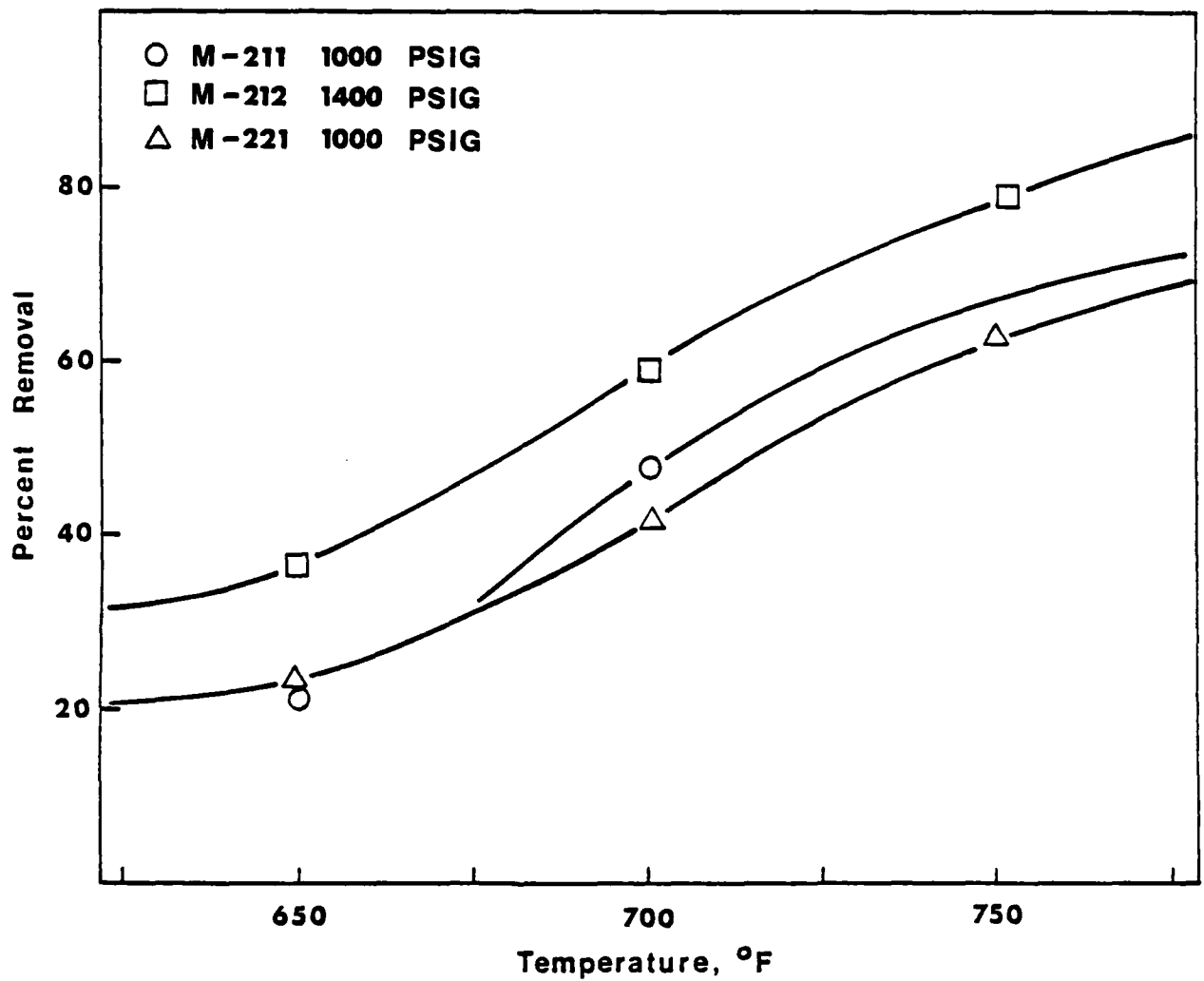
#### DISCUSSION OF RESULTS

The cycle oil hydrotreating of the M-Series above-ground shale oil went very smoothly. No operating problems were encountered and the only real problems arose from insufficient samples and an inability to have as many analyses as necessary to completely characterize the products and effectiveness of this hydrotreating step. A few portions of the material balances, therefore, had to be calculated for completeness.

Enough results were obtained to show that desulfurization was accomplished as had been anticipated. In all runs except the M-221 650°F run, desulfurization was no less than 75 percent and ran as high as almost 94 percent. These results clearly indicate that any fuel oil product stream taken from this unit will easily surpass the military specification of sulfur content at 3.5 weight percent maximum. The viscosity and carbon residues of these product streams are also well below the maximum levels allowed for in military fuel oil. The only military specification for fuel oil that the cycle oil hydrotreated above-ground shale oil product could not meet was the pour point. For all runs the product was 40 to 45°F over the allowed



**Figure VI-3. Cycle Oil Hydrotreating -  
Above-ground Shale Oil - Temperature  
Dependence Of Desulfurization At 1 LHSV**



**Figure VI-4. Cycle Oil Hydrotreating - Above-ground Shale Oil - Temperature Dependence Of Denitrogenation At 1 LHSV**

maximum pour point, as was anticipated, due to the high level of paraffins in the products. This should not, however, adversely affect the value of the fuel oil. Pour depressants would probably be adequate for this situation.

The denitrogenation accomplished by the cycle oil hydrotreating of the M-Series above-ground shale oil ranged from about 22 to 79 percent. Overall it appears that preferred levels of desulfurization and denitrogenation occurred at 700°F, 1400 psig.

If a recycle stream to the FCC is taken off the cycle oil hydrotreater, there should be no problems of any sort. Cracking of the paraffins and partially saturated aromatics in this stream should, in fact, be easier than for the bottoms off the crude shale hydrotreater, and, therefore, the severity of the FCC unit could possibly be lessened. Any sort of further processing on these cycle oil hydrotreated streams should, in fact, present no difficulties.

#### CONCLUSIONS/RECOMMENDATIONS

The operation of the bench scale cycle oil hydrotreater on the M-Series above-ground shale oil shows that shale processed as indicated can be effectively hydrotreated. Even at the relatively mild operating conditions of 650°F, 1000 psig, desulfurization of 60.8 and 75.5 percent can be obtained; however, to achieve significant levels of denitrogenation the unit must operate at a minimum of 700°F, whereas at 1000 psig, 48 and 42 percent

levels of denitrogenation can be obtained and at 1400 psig, a 59 percent level of denitrogenation can be obtained. At this severity desulfurization should reach almost 90 percent.

All military specifications on fuel oil including sulfur content, carbon residue, API gravity, and viscosity can easily be met by the M-Series above-ground shale oil product from the cycle oil hydrotreater. The pour point does not meet specification and heating of the product may have to accompany its use as a fuel oil due to the high paraffin content.. An FCC recycle stream should be taken from this hydrotreating step, since this upgraded and paraffinic product can lead to less severe operation of the FCC unit. Further processing of this product should also be considered.

## SECTION VII

### GUARDCASE HYDROTREATING

The guardcase hydrotreater is provided in the EXTRACT-ACRACKING process for final removal of trace quantities of sulfur, nitrogen, oxygen, and/or metallic contaminants. This process section provides an ultra-pure feedstock for any further processing required downstream.

Two sets of studies were provided during Phase II. In the first study, three samples (from the previously described M-Series) were processed at constant (projected) required conditions. In the second, incremental severity increases were provided to define minimum required severity for a 1 ppm sulfur and nitrogen product, followed by roughly 100 hours or more at single conditions to evaluate catalyst stability.

Products from these studies were fractionated, analyzed and used for further processing.

#### 1. M-SERIES GUARDCASE HYDROTREATING

##### SUMMARY

Samples of above-ground shale oil raffinate which had been produced by crude shale oil hydrotreating, fluid catalytic cracking, and extraction were processed to less than 1 ppm sulfur and nitrogen content in the guardcase module. Initially, problems were encountered which prevented attainment of these product heteroatom specifications, and



a rehydrotreating step was required. These results were postulated, and later proven, to be caused by contamination of the guardcase catalyst by carryover from the extraction process.

#### OBJECTIVES

Objectives for these tests were to: (1) determine the stabilized activity of the selected catalyst for reducing sulfur and nitrogen of pre-jet fuel streams and (2) treat sufficient quantities of shale oil raffinate for further process studies.

#### MECHANICAL DESCRIPTION

The equipment used to guardcase hydrotreat is shown in Figure VII-1. The reactor is 1" I.D., stainless steel and 49" long. Liquid is charged to the reactor by a Lapp diaphragm pump, hydrogen inlet pressure is controlled with a manual Linde regulator, and hydrogen flow is controlled with a Brooks electric valve. Needle valves and a rotameter are used for back-up manual control of hydrogen flow. Hydrogen sulfide is piped to the unit for catalyst sulfiding and nitrogen is provided for purging and pressure testing.

Four controllers adjust electrical heating of the four reactor zones. A small heat exchanger cools reactor effluent; a Grove backpressure regulator controls system pressure and lets down product to near atmospheric pressure. A pressure alarm gauge and electric solenoid protect the product collection system from high pressure.

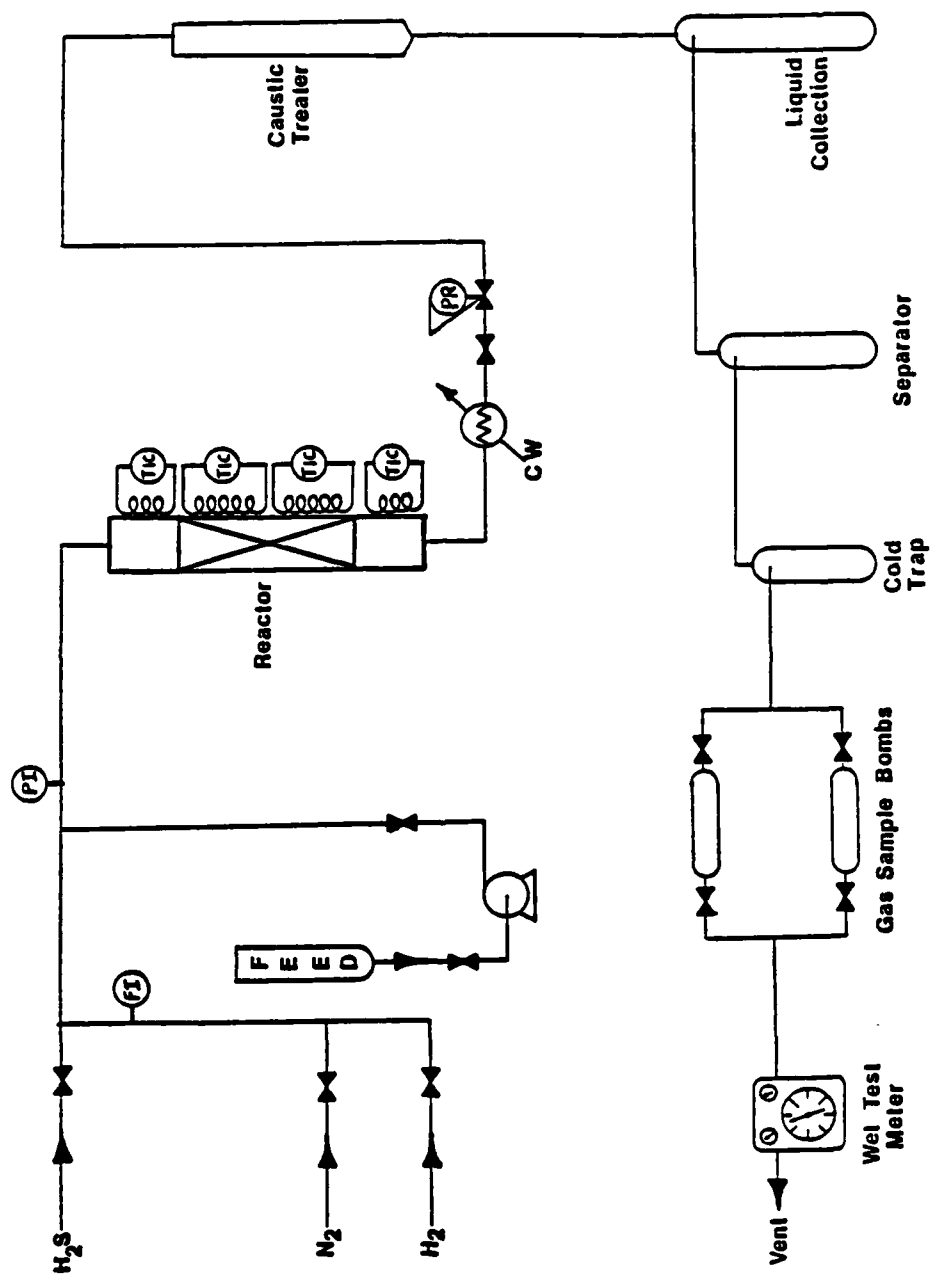


Figure VII-1. Schematic For Guardcase Hydrotreating Set-up

## FEEDSTOCKS

Feedstocks for these runs were raffinates from the extraction process. All samples were prepared as described in earlier M-Series documentation for the crude shale oil hydrotreating, fluid catalytic cracking and extraction studies. In order to study in more detail the impact of processing FCC distillate on the extraction operation, sample M-212 crude hydrotreater distillate and FCC distillate were extracted separately and the guardcase operations were also done separately. These samples are labeled M-212a and M-212b, representing hydrotreated and cat cracked samples respectively. Properties for these feedstocks are presented in Table VII-1.

## DESCRIPTION OF EXPERIMENTAL PROCEDURE

Preparation and Break-in - For initial hydrotreating of M-211, M-212a and M-212b reactors were packed with 50 cc of 1/16" Ni/Mo catalyst and diluted with an equal volume of Ottawa sand in 10-ml increments. Postheat and preheat zones both are filled with inert tab alumina.

For initial treating and retreating of M-221, reactors were packed similarly except 100-ml of catalyst was used. Retreatments of M-211 and M-212 were done consecutively with the same bed used for retreatment of M-221. (The bed was cooled for two hours with hydrogen flow between retreatment runs.

TABLE VII-1

RAFFINATE PROPERTIES-FEED TO  
ORIGINAL HYDROTREATING STUDIES

NUMBER	M-211	M-212a	M-212b	M-221
°API	42.9	42.7	37.6	40.5
SULFUR, WT%	0.19	0.21	0.18	0.19
NITROGEN WT%	0.36	0.42	0.48	0.34

Before operation the units were purged with nitrogen, pressure tested first with nitrogen, then hydrogen to 200 psig greater than run pressure.

Sulfiding the catalyst was accomplished by passing hydrogen sulfide through the reactor at 20 psig. Heaters are started at 200°F and increased 50°F every half-hour until attaining 50°F greater than the highest run temperature. The unit was blocked-in for two hours at the final sulfiding temperature and full H<sub>2</sub>S bottle pressure. After the two hours blocking the reactor was allowed to cool to 400°F and purged for ten minutes.

Catalyst break-in was accomplished as follows:

1. Begin H<sub>2</sub> flow to cold reactor at specified run rate
2. Set temperature controls to 300°F
3. Begin oil flow to reactor at specified run rate
4. Hold at 300°F for one hour, then raise temperatures to 400°F
5. Hold at 400°F for thirty minutes, then raise to 450°F
6. Thereafter raise temperature to 675°F in 50°F increments every thirty minutes

The first four to eight hours were break-in and line-out. Break-in and lineout material were saved.

Each run was continued until the feed nearly ran out (50-ml left). Then the break-in and lineout product was added to the feed reservoir and used until exhausted.

Run #	Material	LHSV (cc/hr)	RUN CONDITIONS		H <sub>2</sub> Pres. (psig)	Catalyst (Vol.)
			SCF(SCF) BBL( Hr)	Temp.		
34	M-211	2(100)	3000(1.88)	675°F	1000	50 cc
35	M-212a	2(100)	3000(1.88)	675°F	1000	50 cc
39	M-212b	2(100)	3000(1.88)	675°F	1000	50 cc
40	M-221	1(100)	3000(1.88)	675°F	1200	100 cc
49	M-221 Rehydrotreat	1(100)	3000(1.88)	700°F	1200	100 cc
50	M-211 Rehydrotreat	2(200)	3000(3.80)	720°F	1200	100 cc
51	M-212a&b Rehydrotreat	2(200)	3000(3.80)	720°F	1200	100 cc

Products from the initial hydrotreating studies were stabilized (as collected) at total reflux for two hours at 300°F pot temperature on an Oldershaw plate distillation column. In order to guard against sulfur recombination, products from rehydrotreating were collected over caustic pellets. The collected liquid from these runs was then water-washed and stabilized on the Oldershaw column in a manner analogous to that used for the initial hydrotreating samples.

#### EXPERIMENTAL RESULTS (INITIAL HYDROTREATING)

The experimental results for Runs M-211, M-212a, M-212b and M-221 are presented below.

Table VII-2 displays the material balances for the M-211 and M-212a; Tables VII-3 AND VII-4 display material balances for the M-212b and M-221.

Table VII-5 shows the fractions into which each run product was fractionated.

#### DISCUSSION

The only major problem encountered during these runs was a water-soluble precipitate which formed in the unit feed buret. This material is postulated to be unremoved acid compounds, and later samples were washed in a more complete manner.

Results from this run are somewhat unexpected in that: (1) high heteroatom concentrations in the products were encountered and (2) apparent extreme catalyst deactivation was observed. This was due to the aforementioned sample contamination.

Since sulfur and nitrogen content of products were greater than the specification necessary for the next processing (reforming), "production" runs were done to hydro-treat the materials.

#### EXPERIMENTAL RESULTS (REHYDROTREATING)

To hydrotreat the M-Series materials to <1 ppm sulfur and nitrogen, the M-211, M-212 and M-221 products were retreated.

All fractions distilled from the original hydrotreating runs were remixed to make M-211, M-212 and M-221 feeds.

TABLE VII-2

## GUARDCASE MATERIAL BALANCE

Sample	M-211		M-212a	
Period	1	2	1	2
OPERATING CONDITIONS				
Temperature, °F	676	675	687	678
Pressure, PSIG	1009	1003	999	1003
LHSV, Hr <sup>-1</sup>	1.92	1.86	1.77	1.62
H <sub>2</sub> Rate, SCFB	3140	3211	3441	3473
MATERIAL BALANCE				
Weight Percent of Feed				
Feed	100.00	100.00	100.00	100.00
H <sub>2</sub> In	5.83	6.11	6.38	6.66
Subtotal In	105.83	106.11	106.38	106.66
H <sub>2</sub> O	-	-	-	-
NH <sub>3</sub>	0.44	0.00	0.50	0.00
H <sub>2</sub> S	0.19	0.00	0.21	0.00
H <sub>2</sub> Out	4.42	4.23	-	-
C <sub>1</sub>	0.20	0.18	-	-
C <sub>2</sub>	0.15	0.15	-	-
C <sub>3</sub>	0.31	0.29	-	-
C <sub>4</sub>	0.14	0.14	-	-
C <sub>5</sub>	0.05	0.05	-	-
Stabilized Liquid	98.01	117.49	95.21	111.82
Subtotal	104.39	122.55	-	-
Closure	98.6	115.5	-	-
Hydrogen Consumption, SCFB	757	984	-	-
PRODUCT PROPERTIES				
°API	47.1	47.1	48.5	48.3
Sulfur, ppm	93	45	110	78
Nitrogen, ppm	12	3	25	1
Oxygen, ppm	-	-	-	-



**TABLE VII-3**

**GUARDCASE MATERIAL BALANCE**

<b>Sample</b>	<b>M-212 b</b>			
<b>Period</b>	<b>1</b>	<b>2</b>	<b>3</b>	
<b>OPERATING CONDITIONS</b>				
Temperature, °F	675	676	675	-
Pressure, PSIG	1013	1025	1022	-
LHSV, Hr <sup>-1</sup>	1.90	1.88	1.72	-
H <sub>2</sub> Rate, SCFB	3572	3581	3951	-
<b>MATERIAL BALANCE</b>				
Weight Percent of Feed				
Feed	100.00	100.00	100.00	-
H <sub>2</sub> In	6.43	6.45	7.24	-
Subtotal In	106.43	106.45	107.24	-
H <sub>2</sub> O	-	-	-	-
NH <sub>3</sub>	0.36	0.36	0.18	-
H <sub>2</sub> S	0.20	0.19	0.00	-
H <sub>2</sub> Out	3.59	6.10	5.22	-
C <sub>1</sub>	0.00	0.00	0.28	-
C <sub>2</sub>	0.24	0.09	0.26	-
C <sub>3</sub>	0.23	0.11	0.30	-
C <sub>4</sub>	0.33	0.09	0.11	-
C <sub>5</sub>	0.00	0.04	0.11	-
Stabilized Liquid	96.69	101.69	107.42	-
Subtotal	101.63	108.58	114.80	-
Closure	95.5	102.0	107.1	-
Hydrogen Consumption, SCFB	1576	194	1103	-
<b>PRODUCT PROPERTIES</b>				
°API	41.0	40.7	41.9	-
Sulfur, ppm	30	137	12	-
Nitrogen, ppm	2000	1900	451	-
Oxygen, ppm	-	-	-	-

TABLE VII-4

## GUARDCASE MATERIAL BALANCE

Sample	M-221			
Period	1	2	3	4
OPERATING CONDITIONS				
Temperature, °F	675	675	675	675
Pressure, PSIG	1219	1210	1195	1204
LHSV, Hr <sup>-1</sup>	0.99	0.97	0.95	0.95
H <sub>2</sub> Rate, SCFB	3007	3068	3136	3150
MATERIAL BALANCE				
Weight Percent of Feed				
Feed	100.00	100.00	100.00	100.00
H <sub>2</sub> In	5.51	5.62	5.74	5.92
Subtotal In	105.51	105.62	105.74	105.92
H <sub>2</sub> O	-	-	-	-
NH <sub>3</sub>	0.41	0.41	0.41	0.09
H <sub>2</sub> S	0.19	0.19	0.19	0.02
H <sub>2</sub> Out	3.11	5.07	5.75	5.89
C <sub>1</sub>	-	-	-	-
C <sub>2</sub>	0.11	0.20	0.13	0.12
C <sub>3</sub>	0.12	0.20	0.11	0.12
C <sub>4</sub>	0.06	0.12	0.07	0.00
C <sub>5</sub>	0.66	0.13	0.08	0.00
Stabilized Liquid	100.13	102.79	99.68	108.25
Subtotal	104.19	109.11	106.43	114.50
Closure	98.8	103.3	100.7	108.1
Hydrogen Consumption, SCFB	1307	300	-	12
PRODUCT PROPERTIES				
°API	45.7	45.1	44.7	45.5
Sulfur, ppm	87	84	139	53
Nitrogen, ppm	12	32	44	23
Oxygen, Wt %	-	-	-	-

**TABLE VII-5**

**FRACTIONS OF GUARDCASE  
HYDROTREATED PRODUCTS**

	<b>M-211</b>	<b>M-212a+b</b>	<b>M-221</b>
<b>Original Hydrotreating</b>	<ul style="list-style-type: none"> <li>• IBP-320°F</li> <li>• 320-540°F</li> <li>• 540°F+</li> </ul>	<ul style="list-style-type: none"> <li>• IBP-520°F</li> <li>• 520°F+</li> </ul>	<ul style="list-style-type: none"> <li>• IBP-320°F</li> <li>• 320-540°F</li> <li>• 540°F+</li> </ul>
<b>Rehydrotreating</b>	<b>Product not cut</b>	<ul style="list-style-type: none"> <li>• IBP-530°F</li> <li>• 530°F+ (diesel)</li> </ul>	<b>Product not cut</b>

The experimental results for retreating M-211, M-212 and M-221 are presented below.

Table VII-6 shows the material balances. Only M-212 product was distilled into cuts; M-211 and M-221 products were not cut, as shown in Table VII-5.

Table VII-7 shows jet fuel property analyses of the M-211, M-212 and M-221 JP-4, JP-8 and broad range products.

### DISCUSSION

The objective of attaining sulfur and nitrogen levels of <1 ppm was achieved. All final M-200 Series products were suitable for reforming tests.

It is noted that the last test period of each run has an unusually high material balance closure. At least part of this is due to operating technique. The last test liquid products were not collected at the end of the test, but after leftover liquid quit draining from the reactor bed.

### CONCLUSIONS

- Product quality specifications of less than 1 ppm sulfur and nitrogen content were met by rehydrotreatment.
- Problems with catalyst activity and activity maintenance were (later) shown to be due to contamination from the extraction process.
- Adequate quantities of product were prepared for further processing through the EXTRACTACRACKING sequence.

**TABLE VII-6**  
**GUARDCASE MATERIAL BALANCE**

Sample	M-221		M-211	M-212	
Period	1	2	1	1	2
OPERATING CONDITIONS					
Temperature, °F	699	700	700	720	731
Pressure, PSIG	1197	1199	1203	1204	1203
LHSV, Hr <sup>-1</sup>	0.967	0.988	1.89	1.92	1.98
H <sub>2</sub> Rate, SCFB	3107	3041	3187	3146	3050
MATERIAL BALANCE					
Weight Percent of Feed					
Feed	100.00	100.00	100.00	100.00	100.00
H <sub>2</sub> In	5.83	5.76	6.06	5.85	5.69
Subtotal In	105.83	105.76	106.06	105.85	105.69
H <sub>2</sub> O	-	-	-	-	-
NH <sub>3</sub>	-	-	-	0.15	-
H <sub>2</sub> S	-	-	-	-	-
H <sub>2</sub> Out	5.75	5.64	5.94	5.95	5.65
C <sub>1</sub>	-	-	-	-	-
C <sub>2</sub>	0.23	0.23	0.21	0.42	0.17
C <sub>3</sub>	0.63	0.61	0.58	0.64	0.38
C <sub>4</sub>	0.58	0.57	0.82	0.56	0.40
C <sub>5</sub>	0.66	0.65	0.37	0.56	0.29
Stabilized Liquid	98.72	105.58	110.75	106.54	104.17
Subtotal	105.58	113.30	118.69	114.83	111.07
Closure	99.8	105.8	111.9	108.5	105.1
Hydrogen Consumption, SCFB	46	61	58	-	21
PRODUCT PROPERTIES					
°API	47.0	47.0	47.7	42.9	43.9
Sulfur, ppm	3	< 1	< 1	1	< 1
Nitrogen, ppm	< 1	< 1	< 1	< 1	< 1
Oxygen, Wt %	-	-	-	-	-

TABLE VII-7

## JET FUEL PROPERTIES OF GUARDCASE PRODUCTS

Product & Fractions*	Freeze Point, °F	%H (wt)	FZA vol % Saturates Olefins Aromatics	ppm S	ppm N	°API at 60 °F	D-86 Distillate (320-540) cut	Viscos. in cSt at 100 & 210 °F	Color	Flash °F	RVP (psia)
M-211 I-320 °F	---	---	---	<1	<1	47.7	(320-540) cut	---	---	---	---
320-540 °F (JP-8)	-51.7°	14.4	S-80.4 O-0.6 A-19.0	---	---	58.4	IBP 342 10% 364 20% 373 50% 398 90% 440 EP 471	---	+16	124°	---
540 °F+	---	14.1	---	---	---	40.8	---	2.83 1.25	---	---	---
M-212 I-520 °F (JP-4)	-59.8° (-41.8° for I-530° cut)	13.9	S-79.6 O-0.7 A-19.7	<1	<1	46.8° (45.5 cut for I- 530° cut)	(I-520) cut IBP 220 10% 294 20% 328 50% 390 90% 451 EP 478	---	RED	64°	0.7
520 °F+	---	13.8	---	---	---	37.2°	---	---	---	---	---
M-221 (Broad Range Fuel) I-320 °F	-19.7°	---	S-88.7 O-0.8 A-10.5	2	<1	47.0	(320-540) cut IBP 360 10% 380 20% 392 50% 434 90% 486 EP 504	---	---	---	---
320-540	---	---	S-78.4 O-0.8 A-19.0	---	---	42.4	---	---	0	---	---
540 °F+	---	---	---	---	---	39.8	---	4.80 1.68	---	---	---

\* Fractions made at 2:1 reflux ratio on a 1" Todd column

- Detailed product properties of each sample produced were developed.

## GC-2 GUARDCASE HYDROTREATING

### SUMMARY

The most important aspect of the GC-2 test was to determine the minimum severity under which shale oil raffinate could be hydrotreated. The GC series raffinates were carefully processed to remove all compounds deleterious to hydrotreating catalyst activity. The GC-2 test confirmed that an uncontaminated shale oil raffinate can easily be treated to reformat feed specifications. The GC-2 catalyst activity showed no apparent deactivation.

The GC-2 feedstock and products were separated into two categories: (1) main portion "ON SPEC" product for further processing and final samples and (2) pseudocomponent fractionation stocks. The pseudocomponents were analyzed for °API, Reid vapor pressure, simulated distillation, viscosity, aromatics and olefins, and freeze point. The pseudocomponent analyses allowed calculation for fractionation and blending to make JP-4, JP-5, JP-8, diesel and gasoline samples from the fully processed GC-2 sample.

### OBJECTIVES

The primary objective of the guardcase hydrotreating study on test series GC-2 was to determine the least severe operating conditions that are required to hydrotreat extracted above-ground shale oil to less than 1 ppm sulfur and

nitrogen levels. This would also determine whether shale not containing complex contaminants from the extraction (GC-2) could be more effectively hydrotreated than shale containing contaminants following extraction (M Series).

Once the least severe operating conditions were found, the study was also intended to provide operation of the hydrotreating reactor at these conditions for an extended period of time to ensure that the desired sulfur and nitrogen levels could be maintained. Sufficient material was hydrotreated to use in later freeze point modification tests and pseudocomponent distillations. The purpose of the pseudocomponent distillations was to acquire data about various boiling range cuts.

#### EQUIPMENT

The experimental set-up for the guardcase hydrotreating of the above-ground shale oil raffinate was identical to that for the hydrotreating of the in situ shale oil raffinate as shown in Figure VII-1. A nominal one-inch trickle flow reactor was operated with downflow of reactants in the actual hydrotreating step. Reactor heating and temperature control was provided by four PID controllers. After the reaction all products passed through a chromatographic separation tube packed with caustic pellets to remove dissolved  $H_2S$ . The liquid product was collected in a glass flask, while the gaseous products passed through a



mist separator and two cold traps before flowing through parallel sampling bombs, a water scrub and a wet test meter, after which these gases were vented.

In the separation of the liquid products into different boiling range fractions, a standard Todd laboratory fractionation column was used with random metal packing in the column.

#### EXPERIMENTAL PROCEDURES

For all runs of test series GC-2 the catalyst bed consisted of 60 cc of a 1/16" Ni/Mo catalyst diluted with 120 cc of Ottawa sand. The catalyst bed was centered in the reactor with catalyst added in 10 cc increments, while the sand was alternately added in 20 cc increments. Inert tabular alumina was used to fill both the postheat and preheat zones.

Three heaters were used to heat the preheat zone, and all three were driven by a thermocouple placed 1" into the top of the catalyst bed. A single heater for the upper portion of the catalyst bed was driven by a thermocouple located 3" into the top of the catalyst bed, while a thermocouple 2" above the bottom of the catalyst bed drove the single heater for the lower portion of the catalyst bed. In the post-heat section of the reactor two heaters driven by a thermocouple at the bottom edge of the catalyst bed.

After assembly of the reactor system was completed, the unit was purged with nitrogen and pressure tested to 200 psig greater than the maximum run pressure, or 1400

psig, first with nitrogen then with hydrogen. Presulfiding followed as  $H_2S$  was passed through the reactor at 20 psig with the heaters set to 200°F. The heaters were raised 50°F every half hour until a temperature of 50°F greater than the highest run temperature, or 750°F, was achieved. Then the unit was blocked in for one hour at this temperature and 20 psig of  $H_2S$ .

With the presulfiding complete the heaters were turned off and the reactor allowed to cool to 300°F with the aid of a nitrogen purge for a half hour. After repressurizing the reactor, catalyst break-in was begun with a nominal hydrogen flow rate of 4000 SCFB (initially 1.51 SCFH). With the temperature controllers on and set to 300°F, feed was initiated to the reactor at a 1 LHSV (60 cc/hr) and the temperature held at 300°F for one hour. The controllers were then raised to 400°F for 30 minutes before being raised to 450°F and thereafter raised to 650°F in 50°F increments every 30 minutes.

Fourteen hours after the completion of the presulfiding, the lineout for Test 1 was ended and the eight hour Test 1 begun. Thereafter, eight hour lineouts preceeded eight hour test periods under the conditions delineated in Table VII-8. When less than 1 ppm sulfur and nitrogen levels were obtained, 24 hour material balances were performed until end of feed. The desired levels were first obtained during Test 4, but due to the delay in getting

TABLE VII-8

**PROCESSING AND CONDITIONS SCHEDULE  
GUARDCASE HYDROTREATING-GC-2  
ABOVE-GROUND SHALE OIL**

**NOTE: Hydrogen rate set to 4000 SCFB for all runs**

TEST NO.	TIME, Hrs.	ITEM	T, °F	LHSV Hr <sup>-1</sup>	P, PSIG
-	0	Packed bed with 1/16" Ni/Mo catalyst; Presulfided	-	-	-
LO-1	0-14	Lineout - Test 1*	650	1	800
1	14-22	Test 1*	"	"	"
LO-2	22-30	Lineout - Test 2*	650	1	1000
2	30-38	Test 2*	"	"	"
LO-3	38-46	Lineout - Test 3*	650	1	1200
3	46-54	Test 3*	"	"	"
LO-4	54-62	Lineout - Test 4*	675	1	1200
4	62-70	Test 4	"	"	"
LO-5	70-78	Lineout - Test 5	700	1	1200
5.1	78-102	First 24 hour balance	"	"	"
5.2	102-126	Second 24 hour balance	"	"	"
5.3	126-150	Third 24 hour balance	"	"	"
5.4	150-174	Fourth 24 hour balance	"	"	"
5.5	174-198	Fifth 24 hour balance	"	"	"
5.6	198-224	Final balance - 26 hours	"	"	"
6.1	224-248	Rerun "offspec" products, First 24 hour balance	700	1.33	1200
6.2	248-262	Rerun "offspec" products, Final balance - 14 hours	"	"	"
-	-	Shutdown	-	-	-

\* Material labeled "offspec" used in Test 6 - Rerun.

analytical results, Test 5 was already underway and so the 24 hour material balances were performed from the beginning of Test 5 until the feed was exhausted.

Following end of feed, as also indicated in Table VII-8, all "OFF-SPEC" product before Test 4, including lineout material, was rerun at the conditions listed. All rerun material and all product collected from the hydro-treating reaction was water-washed three to five times in a separatory funnel with an equal volume of fresh deionized water. The purpose of this was to remove any caustic contaminants entrained in the product stream following passage through the caustic packed tube after reaction. All test and material balance liquid products were also stabilized at total reflux on a fractionation column for two hours at 300°F pot temperature to further remove dissolved  $H_2S$  and  $NH_3$  contaminants from the liquid products. Only after the water washes and stabilization were samples submitted for the various analyses needed to characterize the product.

#### CHEMICAL/CATALYST DESCRIPTION

In the processing of the above-ground shale oil GC-2 in the guardcase hydrotreating step, grade CP hydrogen sulfide ( $H_2S$ ) was used for the presulfiding of the catalyst; the catalyst itself was a nickel molybdate catalyst on 1/16" support. The hydrogen used in the actual reaction was 99.95+ percent pure  $H_2$  and the caustic pellets for removal of  $H_2S$  from the product streams were electrolytic pellets of 97+ percent  $NaOH$  and 0.40 percent  $Na_2CO_3$ . In

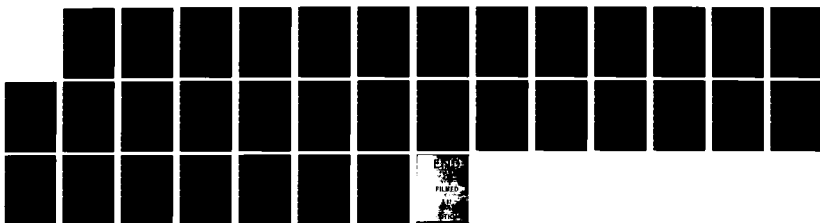
AD-A128 635

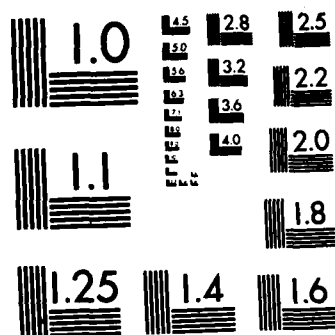
REFINING OF MILITARY JET FUELS FROM SHALE OIL PART II  
VOLUME III ABOVE GR. (U) ASHLAND PETROLEUM CO KY  
H F MOORE ET AL. MAR 82 AFWL-TR-81-2056-PT-2-VOL-3  
F33615-78-C-2080 F/G 21/4

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MICROCOPY RESOLUTION TEST CHART  
NATIONAL BUREAU OF STANDARDS-1963-A

the water washes of the products deionized water was employed.

#### FEEDSTOCK

The GC-2 labeled feed to the guardcase hydrotreater was an above-ground shale oil which, to this point in the experimental scheme of the EXTRACTACRACKING process, had been hydrotreated in the crude shale hydrotreater at the targeted conditions of 675°F, 1000 psig, a 2 LHSV and a hydrogen rate of 3000 SCFB. Four samples of the full range product (PHO-1, 2, 3 and 4) from this first step were cracked in a FCC unit at the targeted conditions of 1000°F riser temperature, 1350°F regenerator temperature and a catalyst-to-oil ratio of 10:1. The IBP to 600°F cut from the product material for each sample was sent to a counter-current, slightly heated extraction column where the PHO-1 sample was extracted with an acid under maximum agitation, and a hydrocarbon-to-acid ratio of approximately 6:1. The PHO-2 sample was extracted under 30 percent agitation and a hydrocarbon-to-acid ratio of 10.2:1. The PHO-3 sample was similarly extracted, while the PHO-4 sample was extracted under 15 percent agitation and the same 10.2:1 hydrocarbon-to-acid ratio. After extraction all four samples were water-washed and recombined to make up the feed GC-2 to the guardcase hydrotreater. The available properties of this combined feedstock are listed in Table VII-9, entitled "Feed Characterization, Guardcase Hydrotreating, Sample GC-2".

**TABLE VII-9**

**FEED CHARACTERIZATION  
GUARDCASE HYDROTREATING  
SAMPLE GC-2**

**Properties:**

<b>°API</b>	<b>39.8</b>
<b>Carbon, Wt %</b>	<b>-</b>
<b>Hydrogen, Wt %</b>	<b>-</b>
<b>Nitrogen, Wt %</b>	<b>0.26</b>
<b>Basic Nitrogen, Wt %</b>	<b>-</b>
<b>Sulfur, Wt %</b>	<b>0.23</b>
<b>Oxygen, Wt %</b>	<b>-</b>
<b>Ramsbottom Carbon, Wt %</b>	<b>-</b>
<b>Aromatics, Wt %</b>	<b>-</b>

**Distillation, °F:**

<b>Wt % By</b>	<b>D2887-73</b>
<b>IBP</b>	<b>155</b>
<b>2</b>	<b>190</b>
<b>10</b>	<b>279</b>
<b>30</b>	<b>377</b>
<b>50</b>	<b>440</b>
<b>70</b>	<b>489</b>
<b>90</b>	<b>547</b>
<b>98</b>	<b>586</b>
<b>EP</b>	<b>651</b>



## RESULTS

The material balances resulting from operation of the guardcase hydrotreater on the GC-2 feed according to the schedule already presented are shown in Table VII-10. The actual time-averaged operating conditions and a few important product properties, particularly the sulfur and nitrogen levels, are also given in the table. The main portion of the water-washed and stabilized product of the guardcase hydrotreating was fractionated into an IBP-580°F boiling range cut for further processing to make jet fuel and also a 580+°F cut which would not be processed further. The pertinent analyses for GC-2 products are shown in Table VII-11.

Samples of the feed and on-spec product were retained for pseudocomponent fractionation into IBP to 290°F, 290 to 400°F, 400 to 510°F, 510 to 570°F and 570°F+ cuts for characterizing these fractions. The jet fuel analyses for each pseudocomponent fraction of the feed are shown in Table VII-12, while those of on-spec product are shown in Table VII-13. The yields for the pseudocomponent fractionations and the simulated distillation analyses for the feed and on-spec product pseudocomponents are also shown in the tables.

## DISCUSSION

All objectives of the run were met. Most important, the shale oil raffinate was successfully hydrotreated to <1 ppm nitrogen and sulfur under conditions of Test 4. Thus,

TABLE VII-10

## GC-2 GUARDCASE MATERIAL BALANCES

Period	1	2	3	4	5.1	5.2
<b>OPERATING CONDITIONS</b>						
Temperature, °F	653	647	648	674	698	697
Pressure, PSIG	798	1000	1201	1200	1200	1203
LHSV, Hr <sup>-1</sup>	.80	.88	.96	.95	.95	.98
H <sub>2</sub> Rate, SCFB	4988	4576	4139	4198	4183	4060
<b>MATERIAL BALANCE</b>						
Weight Percent of Feed						
Feed	100.00	100.00	100.00	100.00	100.00	100.00
H <sub>2</sub> In	9.10	8.35	7.55	7.66	7.63	7.41
Subtotal In	109.10	108.35	107.55	107.66	107.63	107.41
H <sub>2</sub> O	-	-	-	-	-	-
NH <sub>3</sub>	.31	.32	.32	.32	.32	.32
H <sub>2</sub> S	.24	.24	.24	.24	.24	.24
H <sub>2</sub> Out	1.06	6.61	6.12	6.15	5.92	5.40
C <sub>1</sub>	.00	.00	.00	.00	.00	.11
C <sub>2</sub>	.01	.30	.39	.33	.53	.63
C <sub>3</sub>	.03	.53	.51	.44	.96	.71
C <sub>4</sub>	.01	.44	.50	.53	.67	.74
C <sub>5</sub>	.01	1.24	2.13	1.89	1.59	1.78
Stabilized Liquid	90.66	101.75	105.06	103.20	102.80	93.69
Subtotal	92.34	111.50	115.28	113.10	113.02	103.64
Closure	84.63	102.91	107.18	105.05	105.00	96.50
Hydrogen Consumption, SCFB	4407	925	785	827	940	1100
<b>PRODUCT PROPERTIES</b>						
°API	44.9	43.8	44.0	45.2	44.8	44.8
Sulfur, ppm	6.3	1.6	2.1	<1	<1	3.4
Nitrogen, ppm	10.2	3.2	<1	<1	<1	<1

TABLE VII-10 (CONT'D)

## GC-2 GUARDCASE MATERIAL BALANCES

Period	5.3	5.4	5.5	5.6	6.1	6.2
OPERATING CONDITIONS						
Temperature, °F	700	700	703	700	698	699
Pressure, PSIG	1201	1200	1200	1200	1201	1205
LHSV, Hr <sup>-1</sup>	.96	.96	.99	.97	1.29	1.22
H <sub>2</sub> Rate, SCFB	4217	4077	3980	4096	3937	4387
MATERIAL BALANCE						
Weight Percent of Feed						
Feed	100.00	100.00	100.00	100.00	100.00	100.00
H <sub>2</sub> In	7.69	7.44	7.26	7.40	7.41	8.17
Subtotal In	107.69	107.44	107.26	107.40	107.41	108.17
H <sub>2</sub> O	-	-	-	-	-	-
NH <sub>3</sub>	.32	.32	.32	.32	.00	.00
H <sub>2</sub> S	.24	.24	.24	.24	.00	.00
H <sub>2</sub> Out	5.94	5.28	5.45	5.48	6.48	6.63
C <sub>1</sub>	.00	.00	.04	.14	.00	.00
C <sub>2</sub>	.35	.56	.22	.26	.22	.28
C <sub>3</sub>	.44	.71	.31	.30	.32	.58
C <sub>4</sub>	.44	.75	.29	.26	.52	.50
C <sub>5</sub>	.97	1.57	.66	.42	.60	.70
Stabilized Liquid	99.61	100.02	98.94	101.68	108.96	101.59
Subtotal	108.33	109.45	106.48	109.10	117.12	110.28
Closure	100.59	101.87	99.27	101.59	109.03	101.95
Hydrogen Consumption, SCFB	956	1183	992	1052	501	827
PRODUCT PROPERTIES						
°API	44.8	44.8	44.8	44.8	45.3	45.1
Sulfur, ppm	<1	<1	<1	<1	<1	1.2
Nitrogen, ppm	<1	<1	<1	<1	<1	<1

TABLE VII-11

JET FUEL ANALYSES - GC-2  
ON-SPEC PRODUCT

	Freeze Pt. °F	FIA	Sulfur	Nitrogen	°API
ONSPEC					
Whole					44.6
1-580 °F	-34.6°	{S-81.7% O-0.8% A-17.5%	<1ppm	<1ppm	45.4
580 °F+					34.1

TABLE VII-12

TODD PSEUDOCOMPONENTS

GC-2 FEED

	ISP-290 F	290-400 F	400-510 F	510-570 F	570+ F
Wt% yield	10.87	30.73	40.29	18.10	*
API	58.2	44.2	36.9	30.9	-
RVP	-	-	-	-	-
Vis 100 F In cs 210 F	-	1.02 0.70	1.99 1.00	3.64 1.37	-
FREEZE, F	-90	-	-	+13.1	-
PIA Saturates	-	-	-	-	-
Olefins	-	-	-	-	-
Aromatics	-	-	-	-	-
SM-O ISP O-2887	91	217	379	492	-
2%	102	238	391	502	-
10%	155	280	418	516	-
50%	223	345	465	543	-
90%	296	399	513	563	-
98%	343	418	527	576	-
SP	379	446	542	592	-

\* Insufficient Sample

**TABLE VII-13**

**TODD PSEUDOCOMPONENTS**

**GC-2 ONSPEC**

ISP-290 F    290-400 F    400-510 F    510-570 F    570+ F

Wt% yield	13.63	22.14	48.99	12.04	3.19
API	59.5	47.4	41.0	41.1	35.2
RVP	2.0	0.2	0.2	-	-
Vis 100 F In ca 210 F	-	1.08 0.73	1.87 0.98	3.38 1.35	7.00 2.24
FREEZE, F	-90	-90	-36.4	+20.3	-
FIA Saturates	88.7	80.6	80.4	90.2	-
Olefins	0.7	0.8	1.0	1.8	-
Aromatics	10.6	18.6	18.6	8.0	-
SM-O ISP D-2887	99	245	346	487	522
2%	136	261	363	501	545
10%	185	291	388	515	563
50%	249	345	450	547	592
90%	318	389	506	573	755
98%	358	419	523	582	780
EP	399	549	543	594	830

contaminant-free shale oil hydrotreats much easier than did the contaminated shale oil from the M-Series runs.

It was planned to stop increasing reactor severity when the product's nitrogen and sulfur level reached <1 ppm, but Test 5 started before the sulfur and nitrogen results came back for the successful test (Test 4).

#### CONCLUSIONS

All four objectives for the run were met.

- The least severe conditions that were tested for hydrotreating the uncontaminated GC-2 shale oil raffinate to <1 ppm sulfur and nitrogen are the conditions of Test 4 (675°F, 1 LHSV, 1200 psig, 4000 SCF/Bbl).
- The reactor was operated at constant conditions for six days and operated for over 10.5 continuous days total during the run.
- Sufficient "ON-SPEC" GC-2 hydrotreated shale oil was prepared for later processing tests and final samples.
- The uncontaminated shale oil raffinate was successfully hydrotreated to <1 ppm sulfur and nitrogen at less severity than the M-Series raffinate required.

## SECTION VIII

### FREEZE POINT MODIFICATIONS

Yet another unique application of the EXTRACTACRACKING process is the ability selectively to modify the freeze point of shale oil derived jet fuels. While freeze point can be attained in some cases by distillation corrections, modification of the freeze point allows an increased yield of jet fuel under otherwise constant conditions.

Studies performed during Phase II encompassed a simulated prescreening processing of three M-Series samples at conditions defined by the prescreening and an accelerated aging run to determine if the high endpoint feedstock would cause excessive catalyst deactivation. The simulation study has been reported in Volume II of this report and will not be repeated herein.

Products from these studies were fractionated into appropriate boiling ranges and the targeted jet fuel products supplied to aromatic saturation.

#### 1. M-SERIES

##### SUMMARY

Studies were performed, at single conditions determined from the simulation studies described in Volume II of this report, on freeze point modification of one JP-4, one JP-8 and one broad range sample derived from above-ground shale oils. Freeze point reductions of 23.4°F(JP-4),



15.3°F(JP-8) and 36°F(broad range) were obtained at comparable operating conditions, signifying that the heavier JP-8 fraction may require higher severity operations for comparable freeze point reduction effectiveness.

#### OBJECTIVES

Objectives for these studies were to: (1) modify the freeze point of potential Air Force fuel samples, (2) determine the comparison between simulated and actual sample processing response and (3) derive a complete freeze point modification yield structure for each sample.

#### EQUIPMENT AND EXPERIMENTAL

Procedures and equipment utilized for these studies were identical to those described in Volume II, Section VIII of this report.

#### FEEDSTOCK

Feedstocks for these studies were rehydrotreated samples M-211, M-212 and M-221 from the previously described guardcase studies. Guardcase product from M-211 was not fractionated before reforming; the M-212 guardcase product was fractionated to IBP to 530°F before reforming; the M-221 guardcase product was reformed as a broad-range (C<sub>6</sub> to 600°F) feed. Properties of all the as-charged feedstocks from the rehydrotreated guardcase runs are shown on the following page.

	<u>FIA, VOL. %</u>		<u>°API Feedstocks</u>
M-211	S	92.2	47.4
	O	1.2	
	A	6.6	
M-212	S	81.9	45.5
	O	1.7	
	A	16.4	
M-221	S	94.8	47.0
	O	0.6	
	A	4.6	

### RESULTS

Pertinent conditions and material balance data are shown in Tables VIII-1, VIII-2 and VIII-3.

### DISCUSSION

These runs demonstrated the feasibility of modifying turbine fuel freeze point by reforming. The average liquid yield for each material is above 95 percent, as shown below.

#### AVERAGE C<sub>5</sub>+ LIQUID YIELDS

M-211	95.49 Wt. %
M-212 (Periods 1 + 2)	98.43 Wt. %
M-221 (Periods 1 + 3 + 4)	95.60 Wt. %

TABLE VIII-1

M211 REFORMING MATERIAL BALANCE

Period	1				
OPERATING CONDITIONS					
Temperature, °F	850				
Pressure, PSIG	500				
LHSV, Hr <sup>-1</sup>	7.86				
H <sub>2</sub> /HC Ratio SCF/BBL	3155				
MATERIAL BALANCE					
Weight Percent of Feed					
H <sub>2</sub>	1.14				
C <sub>1</sub>	1.04				
C <sub>2</sub>	1.01				
C <sub>3</sub>	1.72				
C <sub>4</sub>	1.37				
C <sub>5</sub>	0.72				
Stabilized Liquid	95.49				
Closure	102.35				
Hydrogen Production, SCFB	576				

**TABLE VIII-2**

**M212 REFORMING MATERIAL BALANCE**

Period	1	2	3	4	
<b>OPERATING CONDITIONS</b>					
Temperature, °F	851	851	851		
Pressure, PSIG	500	500	500		
LHSV, Hr <sup>-1</sup>	8.10	7.90	7.87		
H <sub>2</sub> /HC Ratio SCF/BBL	3061	3139	3151		
<b>MATERIAL BALANCE</b>					
<b>Weight Percent of Feed</b>					
H <sub>2</sub>	1.19	1.38	-		
C <sub>1</sub>	1.00	.72	-		
C <sub>2</sub>	0.89	.45			
C <sub>3</sub>	1.49	.82			
C <sub>4</sub>	1.13	.58			
C <sub>5</sub>	0.63	.20			
Stabilized Liquid	99.47	97.39	96.85		
Closure	105.5	101.4			
Hydrogen Production, SCFB	608	701			

**TABLE VIII-3**

**M221 REFORMING MATERIAL BALANCE**

Period	1	2	3	4	
<b>OPERATING CONDITIONS</b>					
Temperature, °F	851	848	848	850	
Pressure, PSIG	500	500	500	500	
LHSV, Hr <sup>-1</sup>	8.00	7.84	8.00	8.20	
H <sub>2</sub> /HC Ratio SCF/BBU	3100	3163	3100	3024	
<b>MATERIAL BALANCE</b>					
<b>Weight Percent of Feed</b>					
H <sub>2</sub>	1.70	-	1.64	1.41	
C <sub>1</sub>	1.17	-	.43	.50	
C <sub>2</sub>	.68	-	.14	.92	
C <sub>3</sub>	1.44	-	.22	1.67	
C <sub>4</sub>	.62	-	.18	1.17	
C <sub>5</sub>	.52	-	.06	.46	
Stabilized Liquid	93.83	88.47	101.70	91.29	
Closure	97.1	-	104.1	97.6	
Hydrogen Production, SCFB	887	-	856	734	

The M-212 charge material was lightest at IBP to 530°F. The M-211 and M-221 charge materials were both full range materials and had similar average liquid yields.

The materials in order of hydrogen yield are:

M-221 > M-212 > M-211

850-750  
SCF  
BBL

700-600  
SCF  
BBL

575  
SCF  
BBL

Properties of pertinent fractions from the original guardcase hydrotreating runs and the reforming runs are shown in Tables VIII-4 through VIII-6. The properties represent the nominal 310°F+ fraction for M-211(JP-8), the IBP to 530°F for M-212(JP-4) and full range for M-221(broad range fuel).

The JP-4 fraction had a large 23°F freeze point depression with a 20 percent gain in aromatics. The JP-8 target had a lesser freeze depression of 15°F for a 23.5 percent gain in aromatics, indicating the higher boiling materials require higher severity operation than the lighter materials. The full range M-221 has a large freeze point depression of 36°F after reforming. The JP-4 and JP-8 materials display a:

.64 to 1.15°F  $\frac{\text{change}}{\% \text{ aromatics}}$

This compares to a ratio of:

**TABLE VIII-4**

**MILITARY JET FUEL PROPERTIES OF  
SAMPLE M211 (JP-8)**

ITEM	JP4	JP8	PRODUCT FROM		
	SPECIFICATION		Guardcase Hydrocrack	Reformer	Aromatic Saturator
Aromatics	≤ 25% vol		19.0	42.5	22.8
API Gravity	45-57	37-51	47.7	41.4	44.2
% Hydrogen	≥ 13.6% wt			12.9	14.3
Freeze Point °F	-72	-58	-51.7	-67	-68.8
Distillation, D-86 Max					
IBP	-	-	342	350	330
10	-	401	364	366	356
20	293	-	373	380	366
50	374	-	398	404	396
90	473	-	440	466	456
EP	518	572	471	516	492
Distillation, Sim-D					
IBP	-	-		86	257
10	-	367		270	331
20	266	-		315	353
50	363	-		385	408
90	482	-		483	486
EP	608	626		584	587
Flash °F			124		

TABLE VIII-5

MILITARY JET FUEL PROPERTIES  
OF SAMPLE M212 (JP-4)

ITEM	JP4	JP8	PRODUCT FROM		
	SPECIFICATION		Guardcase Hydrocrack	Reformer	Aromatic Saturator
Aromatics	≤ 25% vol		19.7	39.3	24.3
API Gravity	45-57	37-51	47.0	42.3	44.6
% Hydrogen	≥ 13.6% wt			12.5	14.0
Freeze Point °F	-72	-58	-41.8	-65.2	-64.3
Distillation, D-86 Max					
IBP	-	-	220		241
10	-	401	294		309
20	293	-	328		336
30	374	-	390		398
40	473	-	451		466
EP	518	572	478		500
Distillation, Sim-D					
IBP	-	-		91	167
10	-	347		260	283
20	266	-		317	328
30	345	-		406	406
40	482	-		507	499
EP	608	626		611	593



**TABLE VIII-6**

**MILITARY JET FUEL PROPERTIES OF  
SAMPLE M221 (BROAD RANGE FUEL)**

	JP4	JP8	PRODUCT FROM		
ITEM	SPECIFICATION		Guardcase Hydrotr'r	Reformer	Aromatic Saturator
Aromatics	≤ 25% vol		17 (1 to 540°F only)	42.3	33.0
API Gravity	45-57	37-51	47.0	42.6	43.4
% Hydrogen	≥ 13.6%wt			12.8	13.6
Freeze Point °F	-72	-58	-19.3	-55.3	-53.5
Distillation, D-86 Max					
IBP	-	-			225
10	-	401			229
20	293	-			330
50	374	-			402
90	473	-			496
EP	518	572			536
Distillation, Sim-D					
IBP	-	-		82	159
10	-	367		243	275
20	266	-		300	323
50	365	-		405	411
90	482	-		539	529
EP	608	626		660	624

$$\frac{2.4^{\circ}\text{F change}}{\% \text{ aromatics}}$$

for the simulation studies.

#### RECOMMENDATIONS AND CONCLUSIONS

- Freeze point modification was demonstrated for both JP-4 and JP-8 turbine fuels.
- Complete module yield structures were defined, with both samples demonstrating >95 weight percent yield.
- Freeze point reduction for actual shale samples, on a °F per percent aromatics charge basis, is less than half of that demonstrated for simulated (non-fractionated) materials.

#### 2. ACCELERATED AGING

##### SUMMARY

GC-2 guardcase product was reformed under accelerated aging conditions to examine preliminary aging parameters for a selected catalyst system. Results, which would nominally correspond to roughly two months of operation for petroleum naphtha, showed significant aging. Modification of operating conditions will be required for this material.

##### OBJECTIVES

Objectives for this study were: (1) examine, on a preliminary basis, initial catalyst deactivation rates and (2) produce material for further processing.

## EQUIPMENT AND PROCEDURE

Equipment utilized for this study was identical to that used for Part 1 of this study. Experimental procedure was changed so that a smaller catalyst charge could be used at higher throughputs and effective severity to accelerate the aging process. Conditions selected were:

910°F

500 psig

24 LHSV

5:1 Hydrogen:Hydrocarbon Ratio

Under petroleum naphtha reforming conditions, the severity differential provided by these parameters would correspond to approximately two months of commercial operation at 32 hours experimentally on stream. This correlation is not of necessity valid for the shale feedstock used, but does serve to indicate the magnitude of acceleration involved.

## FEEDSTOCK

Feedstock for this run was guardcase product from Run GC-2. The full-range guardcase product was fractionated to a nominal 580°F overhead to remove excessive heavy ends which could cause erroneously high deactivation rates in this study. Properties of the feedstock are shown below.

### REFORMATE STEP FEEDSTOCK PROPERTIES

	<u>FIA</u>	<u>°API = 45.4 @ 60°F</u>
S	81.7% Wt.	Nominally IBP to 580°F
O	0.8% Wt.	Portion of Guardcase
A	17.5% Wt.	Hydrotreater product

### RESULTS

Results for this study are shown in Table VIII-7, as obtained by experimental measurement.

The properties of the composited product versus the feedstock are shown in Table VIII-8.

### DISCUSSION

Some deactivation was observed during the run. Figure VIII-1 presents (normalized) data for hydrogen production, C<sub>5</sub>+ liquid yield and liquid product aromatic content. As the aging occurred, hydrogen yields decreased, liquid product yield remained about the same, and aromatics content decreased as expected. Unfortunately, the supply of feed was exhausted in hour 24 and no further data were obtainable.

The deactivation rates demonstrated appear to be quite unacceptable. Modification of conditions and possibly feedstock will be required for this material.

**TABLE VIII-7**

**GC-2 ACCELERATED AGING  
REFORMING MATERIAL BALANCE**

Period	1	2	3	4	5	Total
<b>OPERATING CONDITIONS</b>						
Temperature, °F	910	910	909	909	-	-
Pressure, PSIG	500	500	500	500	-	-
LHSV, Hr <sup>-1</sup>	23.3	23.7	24.8	24.8	-	-
H <sub>2</sub> /HC Ratio	6269	6163	5877	5774	-	-
<b>MATERIAL BALANCE</b>						
Weight Percent of Feed						
H <sub>2</sub>	0.90	0.96	0.52	-0.07	-	0.56
C <sub>1</sub>	0.97	0.91	0.89	0.71	-	0.87
C <sub>2</sub>	1.58	1.12	2.07	1.58	-	1.59
C <sub>3</sub>	2.18	1.28	2.96	2.20	-	2.16
C <sub>4</sub>	1.34	0.86	1.33	1.30	-	1.21
C <sub>5</sub>	0.52	0.37	0.30	0.36	-	0.39
Stabilized Liquid	93.02	93.20	90.75	88.80	-	91.44
Closure	100.5	98.7	98.8	94.9	-	98.2
Hours on Stream	6	12	18	24	-	24
Hydrogen Production, SCFB	479	508	279	-	-	297
<b>PRODUCT PROPERTIES</b>						
Saturates	54.2	60.3	68.4	68.9	-	-
Olefins	1.4	1.0	0.9	0.9	-	-
Aromatics	44.4	38.7	30.7	30.2	-	38.5

**TABLE VIII-8**

**MILITARY JET FUEL PROPERTIES OF  
SAMPLE M221 (BROAD RANGE FUEL)**

ITEM	JP4	JP8	PRODUCT FROM		
	SPECIFICATION		Guardcase Hydrocrack	Reformer	Aromatic Saturator
Aromatics	≤ 25% vol		17.5	38.5	5.6
API Gravity	43-57	37-51	45.4	42.7	47.4
% Hydrogen	≥ 13.6%wt			13.0	14.5
Freeze Point °F	-72	-58	-34.6	-55.3	-53.5
<b>Distillation, D-86 Max</b>					
IBP	-	-			190
10	-	401			278
20	293	-			310
50	374	-			376
90	473	-			476
EP	518	572			514
<b>Distillation, Sim-D</b>					
IBP	-	-		74	151
10	-	367		240	265
20	266	-		291	311
50	365	-		398	410
90	482	-		523	526
EP	608	626		689	708

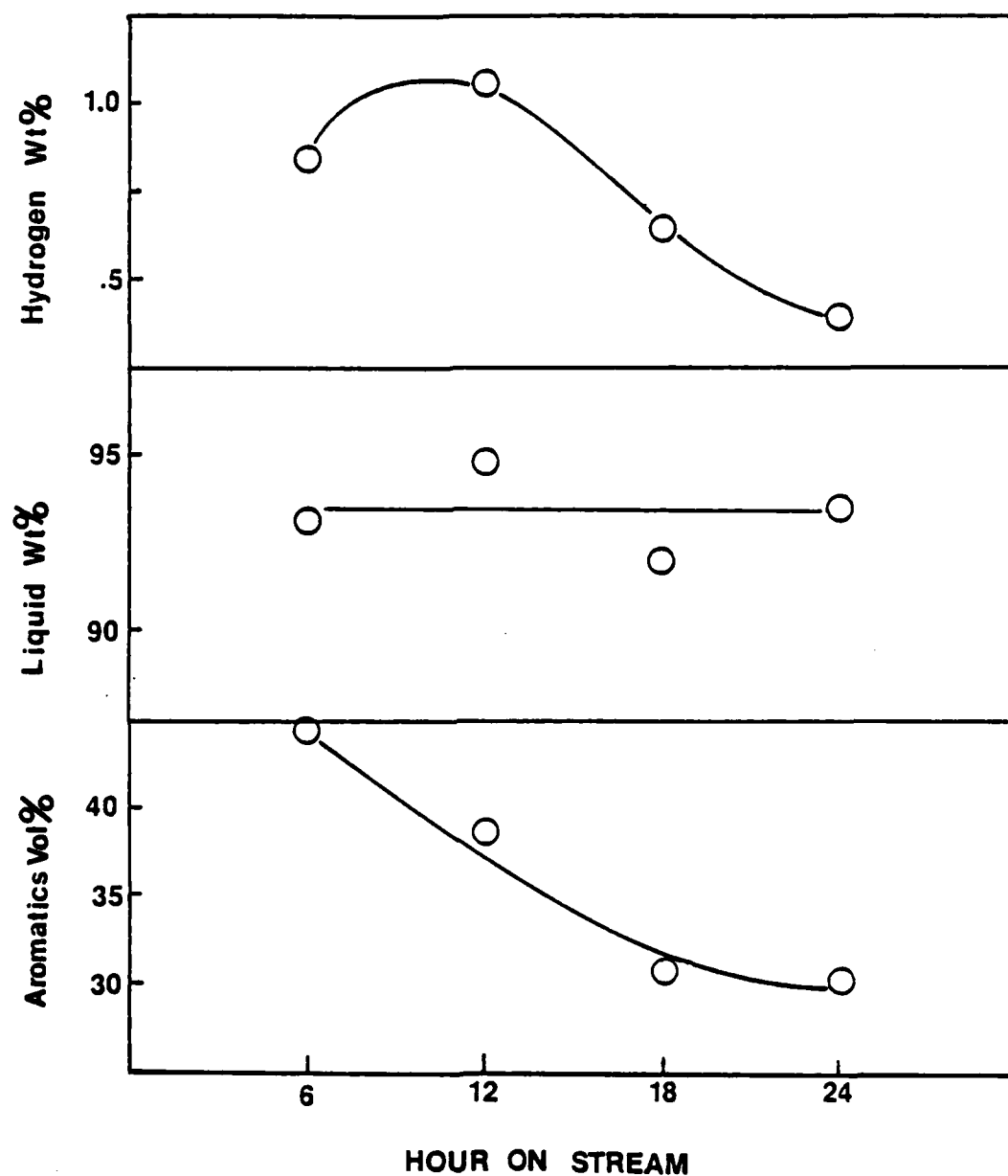


Figure VIII-1. Accelerated Aging Response  
Of Sample GC-2 (Normalized Data)

#### RECOMMENDATIONS AND CONCLUSIONS

- Aging behavior of the freeze point modification module was shown to be unacceptable.
- Sample was produced for further processing.



## SECTION IX

### AROMATIC SATURATION

#### SUMMARY

Ashland's aromatic saturation process has been demonstrated for a total of four samples at conditions estimated a priori to produce potential turbine fuel materials with aromatic contents of less than 25 volume percent. Source samples prepared for blocked-out production of specific turbine fuels (M-Series samples) were saturated to aromatic levels of 22.8 to 33.0 percent. The GC-2 sample, representing a concurrent production mode of all potential turbine fuel types, was processed to a very low 5.6 percent aromatics at conditions analogous to that used for the M-Series samples. While the M-Series showed marginally higher aromatic content in the feed material, there is no direct explanation of this very large difference in saturation efficiency. A total of four potential turbine fuels were satisfactorily produced in this study. Finally, the postulated low impact of saturation on turbine fuel freeze point was demonstrated, with less than 2°F loss of measured freeze point for each sample.

#### OBJECTIVES

The objectives are to: (1) determine the effectiveness of Ashland's aromatic saturation process, (2) determine the freeze point, product properties, and product yield

response to process parameters, and (3) determine the relation between freeze point modification and aromatic saturation for JP-4 and JP-8 fractions.

#### EQUIPMENT

These experiments were performed in a 316SS 1" I.D. Universal reactor heated by a radiant heat furnace. The temperatures were controlled through the use of Thermo Electric Selectral switches and measured by means of Iron-Constantan couples located throughout the reactor (preheat, catalyst bed, postheat) and Honeywell temperature indicator. The feed was metered from a capped (air bleed equalizer) graduate via a Lapp pump. The hydrogen was metered to the reactor through a Brooks continuous flow electronic equalizer. The effluent gas was separated from the liquid product in a Jerguson liquid level gauge and depressured to atmospheric pressure through a Grove pressure regulator. The effluent gas and any light gases from the liquid (after discharging to atmospheric pressure in a closed system) were passed through two acetone-dry ice traps and then measured by means of a wet test meter. The material collected in the dry ice traps and the liquid product were combined and stabilized to a 5°C overhead. Spot gas samples were taken during various periods of the test cycle, submitted for G.C. analysis and the values averaged.

### PROCEDURE

The Universal 1" I.D. reactor was packed with 35 gr (50-ml) of catalyst in a normal downflow pseudologarithmic manner. Tabular alumina was used for preheat and postheat sections. Hydrogen was allowed to flow over the catalyst overnight while the temperature was maintained at 750°F. After reduction of the catalyst, feeds were started and the reaction zone was controlled at 500°F. Hydrogen flow was maintained at 5.2 SCFH. After a two-hour lineout period, product was collected and data were taken until all feed material was used. Refractive index was monitored to confirm activity. The conditions of the runs were as follows:

Temperature:	500°F
Pressure:	200 psig
LHSV:	2.0 (70cc/hr)
H <sub>2</sub> /HC Molar Ratio:	10/1 (5.2 SCFH)

### FEEDSTOCKS AND CATALYST

The feedstocks for aromatic saturation were the M-211, M-212, M-221 and GC-2 products from Section VIII's freeze point modification (reforming). The feedstock FIA and gravity analyses are shown below:

	<u>M-211</u>	<u>M-212</u>	<u>M-221</u>	<u>GC-2</u>
°API @ 60°F	41.4	42.3	42.6	42.7
<u>FIA</u>				
Saturates	55.9	59.4	57.1	60.3
Olefins	1.6	1.3	0.6	1.2
Aromatics	42.5	39.3	42.3	38.5

Other feedstock properties are summarized in Tables VIII-4 through VIII-6. Note that the IBP to 310°F gasoline portion of M-211 (JP-8 target) was removed from the reformate prior to saturation. M-212 and M-221 were taken straight from the reformer to the saturator.

The catalyst is a 1/20" extrudate of platinum on alumina.

### RESULTS

The M and GC series samples were mildly saturated at the conditions outlined in the procedure. The material balances and conditions for the M and GC series are shown in Tables IX-1 and IX-2.

Normalized yields of stabilized liquids are: 100.26 weight percent for M-211; 99.37 weight percent for M-212; 98.75 weight percent for M-221 and 101.19 weight percent for GC-2.

### DISCUSSION

Hydrogen consumption was highest for the broad range M-221 and GC-2 fuels (780 and 1101 SCF/BBL).

TABLE IX-1

# M-SERIES AROMATIC SATURATION MATERIAL BALANCE

Period	M 211		M 212		M 221
OPERATING CONDITIONS					
Temperature, °F	516		510		517
Pressure, PSIG	200		200		200
LHSV, Hr <sup>-1</sup>	2.18		2.02		2.03
H <sub>2</sub> , SCFB	7598		8184		8136
MATERIAL BALANCE					
Weight Percent of Feed					
H <sub>2</sub>	-0.84		-1.45		-0.82
C <sub>1</sub>	-		.24		.00
C <sub>2</sub>	-		.00		.02
C <sub>3</sub>	-		.12		.06
C <sub>4</sub>	-		.77		.25
C <sub>5</sub>	-		1.16		.46
Stabilized Liquid	95.24		96.39		98.47
Closure	94.99		97.61		99.09
Hydrogen Consumption, SCFB	511		780		441
PRODUCT PROPERTIES					
Saturates	76.6		66.5		75.3
Olefins	0.6		0.5		0.4
Aromatics	22.8		33.0		24.3

**TABLE IX-2**

**GC-2 AROMATIC SATURATION  
MATERIAL BALANCE**

Period	1	2	3	4	5	Total
<b>OPERATING CONDITIONS</b>						
Temperature, °F	523	521	519	520	-	521
Pressure, PSIG	200	200	200	200	-	200
LHSV, Hr <sup>-1</sup>	2.03	1.99	2.03	1.95	-	2.00
H <sub>2</sub> Rate, SCFB	8160	8316	8160	8478	-	8279
<b>MATERIAL BALANCE</b>						
Weight Percent of Feed						
Feed	100.00	100.00	100.00	100.00	-	100.00
H <sub>2</sub> In	15.15	115.43	115.15	115.74	-	115.37
Subtotal In	115.15	115.43	115.15	115.74	-	115.37
H <sub>2</sub> O	-	-	-	-	-	-
NH <sub>3</sub>	-	-	-	-	-	-
H <sub>2</sub> S	-	-	-	-	-	-
H <sub>2</sub> Out	12.89	13.21	13.17	14.02	-	13.32
C <sub>1</sub>	.00	.00	.00	.00	-	.00
C <sub>2</sub>	.00	.00	.00	.00	-	.00
C <sub>3</sub>	.20	.23	.06	.06	-	.14
C <sub>4</sub>	.68	.93	.15	.24	-	.50
C <sub>5</sub>	.61	1.11	.00	.20	-	.48
Stabilized Liquid	105.73	106.21	98.65	102.26	-	103.21
Subtotal	120.13	121.71	112.04	116.79	-	117.67
Closure	104.32	105.44	97.29	100.91	-	106.99
Hydrogen Consumption, SCFB	1216	1196	1064	926	-	1101

The target JP-4 (M-212) and JP-8 (M-211) fuels had H<sub>2</sub> consumptions of 441 and 511 SCF/BBL.

All the samples exhibited less than ~2°F change in freeze point, although the change in aromatics content ranged from ~9.3 to ~27.9 weight percentage points.

The product properties are displayed in the same tables as the feedstock properties, Tables VIII-4 through VIII-6 and Table VIII-8.

#### CONCLUSIONS

- Ashland's aromatic saturation process reduced the aromatics content of the jet fuels to below 25 weight percent in three of the four samples.
- No freeze points of the aromatic saturation samples dropped by more than 2°F.

